Patterns of Efficiency and Degradation Measured with Imaging Techniques in Dye Sensitization Solar Cells

B. Macht, M. Turrión*, A. Barkschat, P. Salvador*, H. Tributsch

Hahn-Meitner-Institut, Dept. Solare Energetik, 14109 Berlin, GERMANY

*Depto. de Matemáticas, Universitat de les Illes Balears, 07071 Palma, SPAIN

Space resolved photocurrent measurements with dye sensitization solare cells and a localized setting of starting parameters (e.g. pattern of illumination, additives) allow access to a variety of informations concerning preparation problems, efficiency limitations, and kinetics of photochemical degradation /1/. Experience with a large variety of cells conduced to the following key observation:

- The techniques of nano-TiO_2 preparation are reflected in characteristic microscopic patterns of photocurrent efficiency (e.g. patches, arising from screen printing). Understanding them can help to improve solar cells.
- Dye sensitization cells based on cis-RuII$(LH_2)_2(NCS)_2$ with LH_2 = 2,2'-bipyridyl-4,4'-dicarboxylic acid (Solaronix Inc.) in contact with a 0,5 M LiI / 50mMI_2 , 0.2 M tert-butyl pyridine in acetonitrile show clear patterns of degradation reflecting the patterns of incident solar simulation light. They can be used to distinguish between real photodegradation and light independent, time dependent deterioration within individual cells.
- The electrolyte may gradually bleach and the fill factor decrease due to an increase of the internal resistance of the cell. The reason is believed to be alkalinization of the electrolyte in presence of water impurities and formation of iodate. Some IR data will be presented.
- The sealing of the cell against the environment may pose problems with respect to evaporation of the organic electrolyte (bubble formation) and the influx of water vapor, oxygen, and contaminations from the environment.

These observations are underlined by properly designed experiments. Some implications and requirements for stabilization of the dye sensitization cells are discussed.

Reference

/1/ Turrión, M., Macht, B., Salvador, P., Tributsch, H.: Z. Phys. Chem., 212 (1998) 51-57

Kinetics of Degradation of Dye Sensitization Solar Cells

A. Barkschat, B. Macht, M. Turrion, H. Tributsch
Hahn-Meitner-Institut, Dep. Solare Energetik, 14109 Berlin, Germany

Simulated solar light was passed through linearly graded absorption filters and projected onto dye sensitization cells (cis-RuII$(LH_2)_2(NCS)_2$ with LH_2 = 2,2'-bipyridyl-4,4'-dicarboxylic acid (Solaronix Inc.); 0.5 M LiI, 50 mM I_2, 0.2 M tert-butyl pyridine in acetonitrile). These were operated under short circuit conditions for longer time periods and the change of the photocurrent patterns monitored with photocurrent imaging techniques /1/.The well reproducible experiments show that, with 0.5 M LiI in the electrolyte, the degradation of cis-RuII$(LH_2)_2(NCS)_2$ occurs linearly with the intensity of solar light in the intensity region between 100% and 1%. These results are in conflict with arguments which exclude participation, in degradation mechanisms, of the excited state, due to fast electron injection (claimed safety margin in rate constant of up to 10^8) and count on efficient regeneration of the oxidized sensitizer (claimed safety margin: 10^8 -10^9) /2/. They, on the other hand, support the evidence that long term photodegradation is a realistic phenomenon which has to be investigated and controlled in order to give the dye sensitization cell a long term stability under outdoor conditions. They also underline the relevance of IR - toal reflection data on dye degradation which were obtained at low photocurrent density (10 μAcm^{-2}) and low LiI concentration (10 mM), conditions imposed by the integration of a total reflection crystal (Si) into the dye sensitization cell /3/. In agreement with the kinetics supposed there the rate of degradation of the sensitizer S, or the rate of formation of a degradation product (P) is proportional to the ratio of photocurrent density (I_{ph}) to iodine concentration ($[c]_{I-}$) or correspondingly to the ratio of light intesity $I_{h\nu}$ to iodide concentration.

$$\frac{dS}{dt} = -\frac{dP}{dt} = -k\frac{I_{ph}}{[c]_{I-}} = -k'\,\frac{I_{h\nu}}{[c]_{I-}} \tag{1}$$

The integral lifetime of the dye sensitization cell will, provided the stability of the electrolyte, the confinement of the electrolyte or the penetration of undesired substances through the sealing are not limiting factors, consequently be determined by the number of quanta ($\int I_{h\nu} dt$) required to consume a certain fraction (S_0) or all sensitizing molecules (unrealistic) :

$$\int I_{h\nu} dt = k''\,[c]_{I-} S_0 = k * \frac{rate\ \ of\ \ sensitizer\ \ regeneration}{rate\ \ of\ \ product\ \ formation}[c]_{I-} S_0 \tag{2}$$

The strategies to be followed for prolonging solar cell lifetimes are obvious: to increase the iodide and the dye concentration (exploiting a buffer capacity) to a maximum, to optimize the rate of sensitizer regeneration and to minimize the rate of product formation (mechanism to be analized in detail). For presently investigated dye sensitization cells lifetimes of one to a few years (depending on operation conditions) may not be exceeded (extrapolation to be specified at the meeting).

References

/1/ M. Turrion, B. Macht, P. Salvador, H. Tributsch, Z. phys. Chem. 212 (1999) 51-57
/2/ O. Kohle, M.Grätzel, A.F. Meyer, T.B. Meyer, Advanced Materials 11 (1997) 904-906
/3/ R. Grünwald, H. Tributsch, J. phys. Chem. B 101(1997)2564

Analytical Formula for Dye Sensitization Solar Cell

Helmut Tributsch

Hahn-Meitner-Institut, Dept. Solare Energetik, 14109 Berlin, Germany

Numerical simulations of dye sensitization cells reflect the complexity of mechanism involved, provide overall descriptions, e.g. /1/, but do not give reasonable intuitive access to specific mechanisms involved in determining efficiency or stability. Basing on the experimental observations that the nano-TiO_2/F:SnO_2/I^-/I_3^- electrolyte front contact has to have vectorial properties for efficient operation of the dye sensitization solar cell and plays an active part in generation photoelectrochemical energy, an analytical formula is derived which allows the understanding of the relevance and involvement of a variety of kinetic and cell parameters. Depending on the need for details, the formula can be expanded to include photochemical kinetics and light trapping properties, or contracted and can be used as an intuitive tool for understanding the function and for improving stability and efficiency of dye sensitization cells.

While the electron transfer and recombination rates with the redox electrolyte at the rectifying interface (nano-TiO_2/F:SnO_2/I^-/I_3^- electrolyte) essentially determine the shape of the current voltage characteristics and efficient electron collection, the photochemical kinetics of the sensitizer-nano TiO_2 interface is basically responsible for the generation rate of electrons and thus for limiting efficiency. Both mechanism have to be optimized for optimal performance. Electrons, injected into TiO_2, together with associated counter ions around the nanoparticles diffuse and migrate (like redox species) towards the rectifying junction and positive charges, carried by the electrolyte in the porous structure diffuse into the counter direction. These species enter the equation with the correspondingly adapted diffusion coefficients.

The degree of vectorial character of the nano-TiO_2/F:SnO_2/I^-/I_3^- electrolyte interface (field dependent charge transfer to the front contact versus recombination rate constant with I_2) distinguishes between a low efficient Galvani-type solar cell (efficiency determined by photoinduced chemical potential gradients, no rectifying contact) and a higher efficient 'junction-type' solar cell (dye injected electrons, stabilized by counter charges, separation and collection of charges assisted by junction potential). The real dye solar cell, having not an ideally rectifying front contact, combines both elements, the Galvani-type and the junction type solar cell which could be mutually optimized for maximum efficiency.

Electrochemical and microwave conductivity experiments are presented in support of the model which essentially describes the nano-structured material as a cathodic photoelectrode (electrons donated to the front contact), which is supplied with photoinjected electrons diffusing along (photoinduced chemical potential) and which is kinetically and energetically controlled by the rectifying TiO_2/F:SnO_2/I^-/I_3^- interface.

Reference

/1/ Ferber, J., Stangel, R., Luther, J.: Solar Energy Material & Solar Cells, 53 (1998) 29-54

Electron transport and trapping in dye-sensitized nanocrystalline solar cells

NW Duffy[1], LM Peter[1*], RMG Rajapakse, AB Walker[2] and KGU Wijayantha[1]

Departments of Chemistry[1] and Physics[2], University of Bath, Bath BA2 7AY, United Kingdom

Electron transport in nanocrystalline cells is dominated by trapping and release of electrons from traps, and the contribution of electrical field to the driving force appears to be small. We have shown in previous work that the concept of an effective diffusion coefficient is valid for small amplitude perturbations in the time or frequency domain that are superimposed on a larger steady state component. For large amplitude perturbations, the concept is meaningless. This effective diffusion coefficient, which can be obtained by analysis of the periodic or transient photocurrent response, is intensity dependent. In the case of TiO_2, the diffusion coefficient varies with $I_o^{0.6,}$ whereas for ZnO the variation is close to $I_o^{0.9}$.

The experimental methods used to study the transport of electrons include small amplitude laser pulse excitation superimposed on cw illumination, and small amplitude sinusoidal intensity modulation. The values of the electron diffusion coefficient obtained by the two methods agree well.

We have extended our earlier single trap model of the small amplitude periodic photocurrent resposne to consider the influence of traps distributed in energy within the bandgap of the oxide. The intensity dependence of the electron diffusion coefficient in the case of TiO_2 can be modelled satisfactorily on the basis of an exponential distribution of trapping states. The weakness of his approach is that the distribution becomes a fitting parameter.

In our most recent work, we have obtained the density of states distribution for electron trapping states directly by a novel charge extraction technique that allows determination of the electron occupancy as a function of photovoltage. The experimentally determined distribution has been used in a detailed model of transport and trapping to predict the small amplitude photocurrent response as a function of electron occupancy. Results will be presented for high efficiency DSNC based on TiO_2 as well as for other cells such as ZnO and SnO_2.

* presenting author: e-mail l.m.peter@bath.ac.uk

Kinetics of the back reaction of electrons with I_3^- in dye sensitized solar cells

NW Duffy, LM Peter*, RMG Rajapakse and KGU Wijayantha

Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom

The incident photon flux to current conversion efficiency (IPCE) of dye sensitized nanocrystalline cells (DSNC) is determined by the product of three efficiencies:

- the light harvesting efficiency (determined by dye coverage, particle size and film thickness)
- the net electron injection efficiency (accounting for the back reaction of electrons with oxidized dye)
- the collection efficiency for electrons at the back contact (determined by the rates of transport and back reaction with I_3^-).

Back reaction of photo-injected electrons with I_3^- is a two electron process:

$$I_3^- + 2e \rightarrow 3I^-$$

and it is very slow at TiO_2, SnO_2 and ZnO. By contrast, the I_3^-/I^- redox couple is fast at the platinum counterelectrode. This difference in electron transfer rates is an essential feature of the DSNC. Without differential kinetics, the device would not be able to develop high photovoltages (up to 0.85 V). Platinum surfaces catalyze the reaction by allowing dissociative chemisorption of iodine, so that the electron transfer involves I_{ads}. Iodine is not strongly adsorbed on oxide surfaces, and it seems likely that electron transfer involves an $I_2^{-\cdot}$ intermediate. A plausible reaction scheme is

$$I_3^- \rightarrow I_2 + I^-$$
$$I_2 + e \rightarrow I_2^{-\cdot}$$

followed either by a second electron transfer step

$$I_2^{-\cdot} + e \rightarrow 2I^-$$

or by disproportionation of $I_2^{-\cdot}$

$$2\,I_2^{-\cdot} \rightarrow I_3^- + I^-$$

Either route can lead to decay kinetics that are second order in electron density.

Determination of the mechanism and kinetics of the back reaction requires a method of following the electron concentration under open circuit conditions. In previous work we used IR absorption, but we have now developed a novel method that allows determination of the electron concentration during open circuit decay of the photovoltage following illumination [1]. Experiments using this new approach will be described, and results will be presented for TiO_2, ZnO and SnO_2/ZnO cells. Time-resolved and frequency-resolved methods have also been used to investigate these systems, and the results will be discussed with particular emphasis on the importance of electron transport and back reaction.

Reference

NW Duffy, LM Peter, RGM Rajapakse and KGU Wijayantha (submitted to J Phys Chem B)

* presenting author: l.m.peter@bath.ac.uk.

HIGHLY EFFICIENT TiO_2/DYE PHOTOELECTROCHEMICAL CELL USING A DRY POLYMERIC ELECTROLYTE

A. F. Nogueira, F. Ocampos, W. A. Gazotti and M-A. De Paoli

Instituto de Química, Universidade Estadual de Campinas, Campinas SP, CP 6154 Cep 13083-970 Brazil Phone: +55 19 788 3022 Fax: +55 19 788 3023
e-mail: anafla@iqm.unicamp.br

A great amount of research has been devoted to dye-sensitized photoelectrochemical cells. These solar cells convert solar energy into electricity with an overall efficiency of 10% [1], comparable with photovoltaic cells using a p-n silicon junction with the advantage of the low cost of the materials. The main disadvantage of these cells is that the active interface operates in a liquid medium. The liquid electrolyte employed (usually acetonitrile with I_3^-/I^-) requires a perfect seal of the whole device. Besides the liquid junction seems to compromise the long range durability of the interface.

Recently we presented the first results obtained for a solid-state dye-sensitized photoelectrochemical device using a polymeric electrolyte as a substitute for the liquid electrolyte [2]. The facility of preparation and assemblage of this device encouraged us to improve the electrical parameters. In this work we introduced some changes concerning the polymeric electrolyte and the TiO_2 film to increase the overall efficiency.

The dye sensitized TiO_2 photoelectrochemical cell was assembled with poly(epichlorohydrin-*co*-ethylene oxide (Daiso Co. Japan) filled with NaI/I_2 as electrolyte and *cis*-Bis(isothiocyanate)-bis(2,2´-4,4´-dicarboxylate)ruthenium(II) as dye. The dry polymeric electrolyte presents an ionic conductivity of 1.5 x $10^{-5}\Omega^{-1}cm^{-1}$ at 30^oC, measured by electrochemical impedance spectroscopy. The redox couple is dissolved in a solution of the elastomer in acetone and *cast* on a previously dye-coated TiO_2 electrode.

The incident photon-to-current conversion efficiency (IPCE) curve as function of wavelength resembles the dye absorption spectrum, exhibiting a peak at 520-30 nm with a maximum of 44 %. The current-voltage curve under irradiation of 100 $mWcm^{-2}$ shows an open circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor (*ff*) equal to 0.862V, 2.4 $mAcm^{-2}$ and 0.41, respectively.

The efficiency of this cell, 0.83 % in comparison to liquid electrolyte cells can be explained mainly in terms of the incomplete wetting of TiO_2-dye nanoparticles by the electrolyte. Taking into account that the electrolyte is a dry ionic conducting elastomer we obtained a high ratio of electricity conversion. Recently Grätzel and cols. reported a solid-state cell using an amorphous organic hole transport material as electrolyte with 0.73 % of efficiency. The device depicted in this work has the advantage of easy preparation and handling. It shows a great potential to be developed.

[1] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, **115** (1993) 6382.

[2] A. F. Nogueira and M-A. De Paoli, *Sol. Energy Mater. Sol. Cells., in press*.

[3] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Gratzel, Nature, **395** (1998) 583.

Acknowledgements: FAPESP fellowship (Process No. 98/10567-6) and financial support (Process No. 96/9983-0)

Electrochemical Self-Assembly of ZnO/Dye Thin Films for Dye-Sensitized Solar Cells

T. Yoshida [1], D.Schlettwein [2], T. Oekermann [1], T. Sugiura [1] and H. Minoura [1]

[1] *Gifu University, Graduate School of Engineering, ERES Division, Yanagido 1-1,Gifu 501-1193, Japan*
e-mail; yoshida@apchem.gifu-u.ac.jp / tel. +81-(0)58-293-2593 / fax +81-(0)58-293-2587

[2] *Universität Bremen, Institut für Angewandte und Physikalische Chemie,*
Postfach 33 04 40, D- 28334 Bremen, Germany

Dye-modified semiconductor films play decisive roles in the dye-sensitized solar cells (DSSCs). While efforts have been made for seeking for better combinations of semiconductors and dyes, the method of materials preparation has been limited to the stepwise processing, that is, preparation of porous semiconductor films by colloid coating and heat treatment above 400 °C, followed by dye adsorption from solution. Recently, we have developed a new and simple method to obtain dye-modified ZnO thin films by one-step electrodeposition from aqueous mixed solutions of $Zn(NO_3)_2$ and water-soluble dyes [1-6]. The deposited films were found to perform as sensitized photoelectrodes. This method not only provides an economical and heat-treatment-free synthetic route to the photoactive materials for the DSSCs, but also realizes self-assembly of ordered ZnO/dye structures as consequences of free chemical interactions among the constituent dye molecules and ions during the films growth. The anisotropy of dye adsorption onto different crystal faces of ZnO brings about ZnO growth into specific crystallographic orientations. Also, the adsorption of dyes on ordered inorganic surfaces as well as the intermolecular chemical interaction of dyes leads to formation of ordered dye assemblies. Since the materials prepared by this "electrochemical self-assembly" possess ZnO/dye mixed structures specially chosen by the constituent molecules, ions and atoms, the synergetic effect at the ZnO/dye boundary should be maximized.

Thin films with various dyes such as metal complexes of tetrasulfophthalocyanines (TSPcM, M = Zn(II), Al(III)[OH], Si(IV)$[OH]_2$) [2-4] and organic dyes such as tetrabromophenol blue (TB) [5] or eosinY (EY) [6] have been successfully prepared by this method. Among them, the ZnO/EY thin film shows especially high photoelectrochemical activity, reaching maximum incident photon to current conversion efficiency (IPCE) of ca. 47 %, which is equivalent to the value reported for the same dye adsorbed on TiO_2 films prepared by the usual process. The electrodeposited ZnO/EY film has nano-spaced porous network built up with nano-sized crystals of ZnO. The dye concentration in the film assuming its homogeneous distribution reaches 0.28 M, much higher than that achieved by the usual process (ca. 0.1 M). Therefore, sufficient photon harvesting is achieved at a film thickness below 2 µm, although the film could be further grown owing to its conductive nature. The dyes are not wrapped by ZnO but only exist on the surface of ZnO, because they can be completely desorbed by alkaline without destroying ZnO. These unique features of the electrochemically self-assembled ZnO/EY film made it possible for the loaded EY molecules to perform as efficient sensitizers.

The electrochemical analysis in the $Zn(NO_3)_2$ + dye mixtures revealed existence of at least two kinds of mechanisms for the dye loading during electrodeposition. Dyes such as TSPcM are simply adsorbed on the growing surface of ZnO, thus yielding colored ZnO films (passive mechanism). However, TB, EY and other xanthene dyes are reduced when the deposition is carried out at potentials below that of the dye reduction (active mechanism). The freshly prepared films are colorless and regenerate the color of the dyes when they are dried in air. The passive mechanism does work for these dyes when the more positive potentials are used. The reduction potential of the dyes shifted positively upon increasing the strength of Zn^{2+}, not NO_3^-, indicating Zn^{2+}-coupled reduction of dyes during the active loading of the dyes. The mechanism of electrochemical self-assembly of ZnO/dye films will be further discussed in the presentation.

1. T. Yoshida and H. Minoura, *Adv. Mater.*, submitted.
2. T. Yoshida, K. Miyamoto, N. Hibi, T. Sugiura, H. Minoura, D. Schlettwein, T. Oekermann, G. Schneider and D. Wöhrle, *Chem.Lett*. **7** (1998) 599.
3. T. Yoshida, M. Tochimoto, D. Schlettwein, D. Wöhrle, T. Sugiura and H. Minoura, *Chem. Mater*., **11**, (1999) 2657.
4. D. Schlettwein, T. Oekermann, T. Yoshida, M. Tochimoto, H. Minoura, *J.Electroanal.Chem.* **481** (2000) 42.
5. T. Yoshida, J. Yoshimura, M. Matsui, T. Sugiura and H. Minoura, *Transactions of the Materials Research Society of Japan*, **24**, (1999) 497.
6. T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura and H. M inoura, *Adv. Mater*., submitted

Localized performance decline within dye-sensitized solar cells

Shinji Koike, Bernd Macht, Axel Barkschat, Toshihko Matsuda†,
Hajime Matsumoto†, Pedro Salvador‡ and Helmut Tributsch

Dept. Solare Energetik, Hahn-Meitner-Institut, Glienicker Str. 100, 14109 Berlin, Germany
†Dept. for Energy Conversion, Osaka National Research Institute, AIST
1-8-31 Midorigaoka, Ikeda, Osaka 563 - 8577, Japan
‡Dept. Mathemáticas e Informática, Universidad de las Islas Baleares, 07071 Palma, Spain

Dye-sensitized solar cells (DSC) are promising energy devices based on unique principles simplifying processes in natural photosynthesis. A sunlight-to-electricity conversion efficiency of 10% has been achieved under the AM 1.5 standard solar spectrum [1]. The Scanning Microscope for Semiconductor Characterization (SMSC) is a light spot technique that allows obtaining images of different photoinduced effects such as photocurrent, photovoltage and electroreflectance. The SMSC was applied to the DSC and revealed photoinduced dye degradation [2].

Here, we present the localized performance decline of the DSC caused by some chemicals using the SMSC technique.

Dye-sensitized solar cells were prepared as follows: TiO_2 powder (P25, Degussa AG) coating with dye (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)- ruthenium(II)), supported by the conducting glass plate was separated from counter electrode (Pt deposited fluorine-doped SnO_2 glass plate) by sealing film (surlyn 1702, DuPont). The electrolyte consisted of 0.3M LiI + 0.03M I_2 in acetonitrile and was filled into the cell by generating a vacuum for injecting the electrolyte through a small opening. The opening was then closed by epoxy resin (Torr Seal®).

The SMSC measurements were carried out usual way [2].

Fig. 1(a) shows the SMSC profile of the DSC finishing under air. There is a reduced photocurrent region close to the electrolyte introducing point. The current reduction is apparently caused by chemicals from outside atmosphere which entered the DSC before sealing such as oxygen and water or the sealing material itself (Torr Seal®). Fig. 1(b) shows the SMSC profile of the DSC, closing the last opening under Ar atmosphere. The reduced current region is also observing in the same place of Fig. 1 (a) but the profile is different. Obviously the sealing material affected localized current reduction of the DSC but the ambient air (e.g. oxygen and humidity) shows an additional effect. This technique could be used to study systematically the effect of chemical or dye sensitization cell performance.

(a) (b)

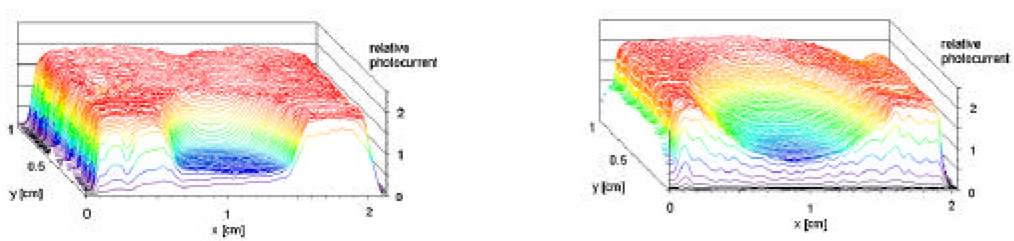


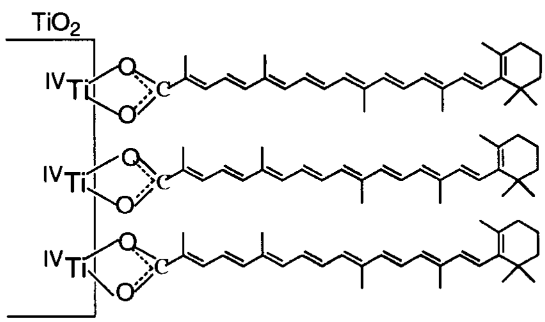
Fig. 1 SMSC profiles of the DSC closing the last opening under air(a) and Ar atmosphere (b).

[1] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.*, **115,** 6382(1993)
[2] M. Turrion, B. Macht, P. Salvador, H. Tributsch, *Z. Phys. Chem.*, **212,** 51(1999)

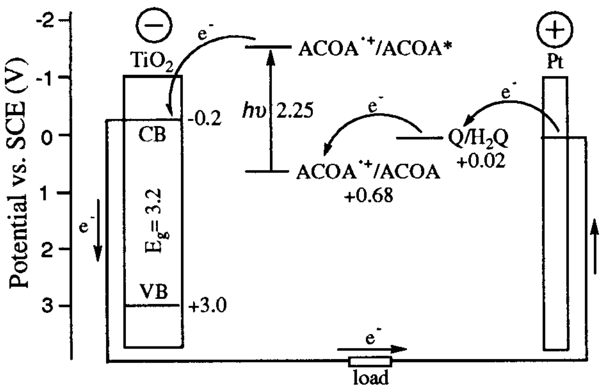
Photocurrent Response for a Carotenoid-sensitized TiO_2 Nanocrystalline Mesoporous Membrane

Frank G. Gao,† Allen J. Bard† and Lowell D. Kispert‡*
† Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78712, and ‡ Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487

Photovoltaic currents are generated upon illumination of ITO electrodes coated with a TiO_2 nanocrystalline mesoporous film and with the covalently bonded carotenoid 8'-apo-β-caroten-8'-oic acid (ACOA) as the sensitizer in an electrochemical cell containing an aqueous electrolyte solution of hydroquinone. A short-circuit photocurrent of 4.6 $\mu A/cm^2$ upon 426 monochromatic illumination at 40 $\mu W/cm^2$ with an IPCE of 34 % and an open-circuit photovoltage of 0.15 V was observed. The photocurrent and photovoltage were stable during 1 h continuous irradiation. The action spectrum resembled the absorption spectrum of ACOA bound on the TiO_2 coating with a maximum near 426 nm. This work is supported by the Division of Chemical Science, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.



Possible Structure
of ACOA Complexes on the TiO_2 surface



Schematic Representation
of the Principle of Carotenoid-sensitized
TiO_2 Photovoltaic Response

Charge Transfer Emission in Dye Sensitized TiO_2 Nanoparticle : A New Approach to Determine of Back Electron Transfer Rate

Hirendra Nath Ghosh

RC & CD Division, Bhabha Atomic Research Centre, Mumbai - 400 085, India

Email : hnghosh@magnum.barc.ernet.in , Fax : 00-91-22-5505151

Interfacial electron transfer (ET) between molecular adsorbate and semiconductor nanoparticles is an intense area of current research work. The present investigation reports the study of electron injection from adsorbed coumarin 343 (C-343) and 7-diethylaminocoumarin-3-carboxylic acid (coumarin D-1421) dyes to TiO_2 nano particles and the subsequent back electron transfer confirmed by picosecond transient absorption studies, where the coumarin cation and the electron in the nanoparticles have been detected in the visible region. After the injection of an electron from excited coumarins to nanoparticle, emission of coumarins get quenched. But when the injected electrons come back to the parent cations, it gives a red shifted low quantum yield charge transfer (CT) emission. Estimation of these CT emission lifetimes directly give the measure of the back electron transfer at the surfaces. This approach to determine back electron on nanoparticle surface is been reported for the first time[1]. From the CT emission spectra it is confirmed that back electron transfer from the conduction band to the parent cation starts before relaxing it down to the conduction band edge or to the trap states. This seems to be the first direct experimental proof. A trial has been given to verify the Marcus inverted regime for the back electron transfer reaction on the semiconductor nanoparticle surface.

References :

(1) H.N.Ghosh. *J.Phys.Chem. B.* **1999**, *103*, 10382.

Conversion of visible light into electricity by dye sensitized solar cell

S.Anandan# and P. Maruthamuthu*
Department of Energy [Chemistry-Interdisciplinary]
University of Madras, Guindy Campus, Chennai 600 025.
India
E-Mail: pmuthu@unimad.ernet.in **Fax: 91-044-2352494**

In the recent years, various methods are used to fabricate solar cells to convert visible light into electricity. Among such cells, dye sensitized solar cells are becoming increasingly popular. The efficiency and the longevity of the cell prepared are found to depend upon the stability of the dye used. This paper deals with the preparation, characterization and use of the dye, $[Ru(Dcbpy)_2(Dpq)]Cl_2.3H_2O$ in the fabrication of solar cell to generate photocurrent. The dye absorbs almost all the visible portion of the light which is the main thrust in the photoconversion study. Solar cells were fabricated with different types of conducting glasses, fluorine doped SnO_2, Indium doped SnO_2 and ZnO doped SnO_2, over which wide band gap semiconductor TiO_2 is coated. Approximately 3×10^{-4} M of dye (in ethanol solvent) was made to adsorb on the TiO_2 coated glass. This material is used as photocathode and Platinum coated conducting glass, prepared by ion beam sputtering method, was used as photoanode. Making use of these two plates, photocells were constructed with I_2/I_3^- as electrolyte. The current conversion efficiencies, I_{sc} and V_{oc} were measured from I-V curves. From the performance of the cells for the conversion of solar radiation into electricity, the efficiency was found to be high for SnO_2 coated conducting glasses and the current generated using this inorganic dye sensitization technique is quite high compared to the *cells* which involve organic dyes.

Bilayer Nanoporous Electrodes for Dye Sensitized Solar Cells

A. Zaban, S. Chen and S. Chappel
Chemistry Department, Bar-Ilan University, Ramat-Gan, 52900, Israel

The high light to energy conversion efficiencies achieved with dye sensitized solar cells may be attributed to the nanoporous TiO_2 electrodes[1]. The properties of these porous semiconductor electrodes are strongly influenced by several factors: the open structure of the electrodes that permits electrolyte penetration through the entire electrode; the magnification of surface properties; the small size of the individual colloidal particles that cannot support a high space charge; and the low inherent conductivity of the semiconductors used. In other words, the porous geometry introduces special characteristics that differentiate these electrodes from their compact analogues. Since the introduction of the nanoporous TiO_2 electrodes, various semiconductors such as SnO_2,[2] ZnO,[3] $SrTiO_3$[4] and Nb_2O_5[5] have been examined for this application including mixtures of materials[6,7]. However, the basic design of the electrodes was not changed.

We report here the fabrication of a bilayer nanoporous electrode and its application in dye sensitized solar cells. The new electrode is designed to solve one of the major disadvantages of the nanoporous electrodes; the absence of a space charge layer and thus the absence of an electric field at the electrode surface. The latter significantly affects the performance of the electrode in dye sensitized solar cells especially with respect to the electron collection efficiency. The new electrode consists of a nanoporous TiO_2 matrix that is covered with a thin layer of Nb_2O_5 (Figure 1). Since the conduction band potential of the Nb_2O_5 is ca. 100 mV more negative than that of the TiO_2 [5]it generates an energy barrier that resembles the band banding in bulk materials. When used in a dye sensitized solar cell the new bilayer electrode performs better than a comparable single material electrode mainly with respect to the collection efficiency. A detailed description of the electrode fabrication characterization and operation will be presented.

References:

1) Nazeeruddin, M. K.; Pechy, P.; Gratzel, M. *Chem. Commun.* **1997**, 1705.
2) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490-4493.
3) Hoyer, P.; Weller, H. *J. Phys. Chem.* **1995**, *99*, 14096-14100.
4) Burnside, S.; Moser, J.-E.; Brooks, K.; Gratzel, M.; Cahen, D. *J. Phys. Chem. B* **1999**, *103*, 9328 -9332.
5) Sayama, K.; Sugihara, H.; Arakawa, H. *Chem. Mater.* **1998**, *10*, 3825-3832.
6) Bedja, I.; Hotchandani, S.; Kamat, P. V. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1997**, *101*, 1651-1653.
7) Tennakone, K.; Kumara, G.; Kottegoda, I. R. M.; Perera, V. P. S. *Chem. Commun.* **1999**, 15.

Dual Electron Injection from Charge-Transfer Excited States of TiO_2-Anchored Ru(II)-4,4' –Dicarboxy-2,2'-Biquinoline Complex

H. Arakawa, A. Isram, K. Hara, H. Sugihara

National Institute of Materials and Chemical Researches. 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

There has been an increasing interest in dye-sensitized solar cells. Grätzel reported solar cells of remarkably high energy conversion efficiency (exceeding 10%) based on a porous TiO_2 semiconductor electrode sensitized with Ru-based polypyridyl-type complexes, such as so-called N3 dye and black dye.[1] We have developed a new class of Ru complexes having 4,7-dicarboxy-1,10-phenanthroline (dcphen). Photosensitization of nanocrystalline TiO_2 electrode by $Ru(dcphenH)_2(NCS)_2(TBA)_2$ showed a high incident photon-to-current conversion efficiency (IPCE:70% at 540 nm). The overall efficiency of 6.1% was obtained at AM-1.5 ($100 mW/cm^2$).[2] We synthesized, furthermore, other new Ru dyes having a wide absorption at longer wave length region, that is, $Ru(dcbiq\underline{H})_2(NCS)_2(TBA)_2$ ($dcbiq\underline{H}_2$ =4,4´-dicarboxy-2,2´-biquinoline) (**I**) . Here, we report a direct observation of efficient electron injection from an ultra-short-lived, higher lying MLCT excited state of complex **1** into the conduction band of TiO_2, suggesting electron injection occurs near the subpicosecond domain.

The complex **1** was synthesized from $Ru(dcbiq\underline{H})_2Cl_2Na_2$ according to the literature. The absorption spectrum of complex **1** in ethanol shows two intense intraligand π-π^* transitions between 250 and 400 nm and two MLCT bands with maxima at 630 nm (ε = 9800 $dm^3\ mol^{-1}\ cm^{-1}$) and 500 nm. The emission lifetimes of lowest excited MLCT state at 880 nm of complex **1** in ethanol-methanol at 298 K and 77 K are 34 ns and 590 ns, respectively. The cyclic voltammogram of complex **1** shows one quasi-reversible wave at 0.92 V *vs*. SCE for the $Ru^{3+/2+}$ couple. A ligand-based reduction potential was observed at -0.85 V *vs*. SCE. Coating of TiO_2 and SnO_2 nanocrystalline films with complex **1** was carried out by soaking the films in a 10^{-4} M ethanolic solution. Photoelectrochemical experiments of the dye sensitized electrode films were performed using a sandwich-type solar cell in conjunction with a redox electrolyte consisted of a solution of 0.6 M dimethylpropyl-imidazolium iodide, 0.05 M I_2, 0.5 M *tert*-butylpyridine, 0.1 M LiI in methoxyacetonitrile. A short-circuit photocurrent of 2.5 mA cm^{-2} for TiO_2 film and 2.12 mA cm^{-2} for SnO_2 film were obtained under simulated AM 1.5 solar irradiation.

It was observed that in the complex **1**-sensitized TiO_2 film, a relatively efficient injection (IPCE $\approx$20%) occurs from the higher lying excited MLCT state ($\lambda_{max} \approx$ 550 nm, adsorbed dye) but injection is much less efficient (IPCE $\approx$3%) from the lowest excited MLCT state ($\lambda_{max} \approx$ 700 nm, adsorbed dye). The IPCE spectrum for complex **1** on SnO_2 film, which has a conduction band edge ~0.5 V more positive than TiO_2, qualitatively trace the dye's absorbance feature and the cell efficiency (IPCE) increased to 10% at 670 nm. These results indicate that the lowest excited MLCT state is energetically allowed to enable transfer of an electron into the conduction band of SnO_2 but not into TiO_2. Thus, dual injection from the metal-to-ligand charge transfer excited states observed in the complex **1**-sensitized TiO_2 film indicates an ultrafast rate of electron injection to TiO_2, and agrees with the findings of femtosecond dynamical studies.

References

1) B. O'Regan and M. Grätzel, *Nature*, **353,** 737 (1991).
2) H. Sugihara, L. P. Singh, K.Sayama, H. Arakawa, et al., *Chem. Lett.,* **1998**, 1005.

ENVIRONMENTAL ASPECTS OF ELECTRICITY GENERATION FROM A NANOCRYSTALLINE DYE SENSITIZED SOLAR CELL SYSTEM

Helena Greijer [a b], Lennart Karlson [b], Sten-Eric Lindquist [a], Anders Hagfeldt [a]*

[a] Department of Physical Chemistry at the University of Uppsala, 751 21 Uppsala, Sweden
[b] ABB Corporate Research, 721 78 Västerås, Sweden
* Corresponding author

Abstract

A Life Cycle Assessment, LCA, of a nanocrystalline dye sensitized solar cell (ncDSC) system has been performed, according to the ISO14040 standard. In brief, LCA is a tool to analyse the total environmental impact of a product or system from cradle to grave. Six different weighing methods were used to rank and select the significant environmental aspects to study further. The most significant environmental aspects according to the weighing methods are emission of sulphur dioxide and carbon dioxide. Carbon dioxide emission was selected as an environmental indicator depending on the growing attention on the global warming effect. In an environmental comparison of electricity generation from a ncDSC system and a natural gas/combined cycle power plant, the gas power plant would result in 450 g CO_2/kWh and the ncDSC system in between 19-47 g CO_2/kWh. The latter can be compared with 42 g CO_2/kWh, according to van Brummelen et al., for another thin film solar cell system made of amorphous silicon. The most significant activity contributing to environmental impact over the life cycle of the ncDSC system is the process energy for producing the solar cell module. Secondly comes the components; glass substrate, frame and junction box. The main improvement from an environmental point of view of the current technology would be an increase in the conversion efficiency from solar radiation to electricity generation and still use low energy demanding production technologies. And the amount of material in the solar cell system should be minimised and designed to maximise recycling.

Degradation mechanisms of nanoporous dye sensitized solar cells

Helena Greijer [a], Jan Lindgren [b], Anders Hagfeldt [a]*

[a] Department of Physical Chemistry at the University of Uppsala, 751 21 Uppsala, Sweden
[b] Department of Chemistry at the University of Uppsala, 751 21 Uppsala, Sweden
* Corresponding author

Abstract

A method for detecting degradation mechanisms of the working electrode in the nanoporous dye sensitized solar cell was developed. The dye, bis(tetrabutylammonium) cis-di(thiocyanato) bis(2,2'-bipyridine-4-carboxylic acid, 4'-carboxylate) ruthenium(II), called N719, adsorbed to the nanostructured TiO_2 was studied with ultraviolet-visual spectroscopy and infrared spectroscopy after being impacted with visual radiation, ultra-violet radiation and humidity, with and without electrolyte and with increased temperature. Most experiments were made in oxygen- and water free atmosphere in an argon containing glovebox. For the UV-VIS experiment, the absorption maxima around 400nm and 547nm, originating from the metal to ligand charge transfer (MLCT) in the dye, were studied. For the infrared spectroscopy the functional groups carboxylic acid (-COOH), carboxylate ($-COO^-$) and thiocyanato (-NCS), could be detected with absorption peaks at 1722 cm^{-1}, 1650-1550 cm^{-1} and 1450-1350 cm^{-1}, and 2100 cm^{-1}, respectively. The amount of the thiocyanato group on the dye molecule decreased when the dry working electrode had been illuminated with UV radiation or been impacted with high temperature (135°C). The amount of the thiocyanato group on the dye molecule also decreased upon illumination of working electrodes in water containing electrolyte with either visual or ultraviolet radiation. The amount of the carboxylic acid group on the dye increased relative to the carboxylate group when dry working electrodes had been impacted with 200°C. The increase of the carboxylic acid group on the dye could be due the breaking of bonds between the TiO_2 and carboxylate group. Preliminary results using Raman resonance scattering will also be discussed at the conference.

Direct Observation of Ultrafast Electron Injection and Recombination in Fluorescein 27-Sensitized TiO_2 Thin Films

Gabor Benkö, Arkady P. Yartsev, Marcus Hilgendorff and Villy Sundström
Department of Chemical Physics, Lund University, Box 124, 22100 Sweden

Electron injection and recombination dynamics of the dye fluorescein 27 adsorbed to a titanium dioxide (TiO_2) thin film in CH_3CN was studied by femtosecond pump-probe spectroscopy. After excitation of the dye at the maximum of absorption transient absorption, spectra and kinetics were recorded in the spectral region between 400 to 2000 nm. It was found that the whole positive transient spectrum is dominated on early time by an induced excited state absorption (ESA). Even in the near-IR spectral region where the ESA of the dye in aqueous solution is less than the noise level of our measurements a pronounced ESA of the dye/TiO_2 system has been observed. Electron injection from the dye molecule into the conduction band of the semiconductor consists in formation of photoproducts, which are conduction-band electrons in TiO_2 and oxidized fluorescein 27 dye molecules. The dynamics of photoproducts can be resolved only at the narrow spectral regions where ESA is cancelled by either stimulated emission signal (SE) or is compensated by ground state absorption bleach at earlier time. The kinetics of SE decay and the rise times of induced absorption of photoproducts are ultrafast and nonexponential. The best fit to the experimental data of SE decay requires the following time constants and initial amplitudes (in parentheses): <0.1 ps (~30%), 0.9 $\pm$ 0.2 ps (~50%), and 7.0 $\pm$ 1.0 ps (~20%). Recombination is also nonexponential, a part of the oxidized dye molecules recombines in ~tens of picoseconds, but the major part of the recombination does not occur on the investigated time scale (until 500 ps).

Having such a dye/TiO_2 system system, by changing its characteristics such as solvent, TiO_2 particle size, etc. the charge transfer rates can be optimized.

Photosensitization of nanocrystalline TiO_2 films with Pt(II)diimine dithiolate complexes

A. Islam, H. Sugihara, K. Hara, L. P. Singh, R. Katoh, H. Arakawa

National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Photoelectrochemical systems with dye-sensitized metal oxide semiconductor electrodes have allowed the construction of low-cost photovoltaic devices over past two decades. Several organic dyes and transition metal complexes of Ru(II),[1] Os(II) and Fe(II) were employed in the solar cells to sensitize nanocrystalline metal oxide semiconductors. So far, the most successful sensitizers employed in these devices are diimine complexes of ruthenium(II) anchored to nanocrystalline TiO_2 films, yielding overall AM1.5 solar to electric power conversion efficiencies of up to 11%. Octahedral charge transfer transition-metal complexes are found attractive sensitizers due to their favorable photophysical properties.

Eisenberg and co-workers investigates intensively the excited state of square planar platinum(II) diimine dithiolate complexes, Pt(NN)(SS), over the past decade. These complexes have a long lived MLCT excite state, which is emissive in fluid solution at ambient conditions and undergo electron transfer quenching both oxidatively and reductively. Although square planar platinum(II) diimine dithiolate complexes represent promising properties for charge transfer sensitization, never have been tried in solar cell application till today.

We present an efficient photosensitization of nanocrystalline TiO_2 films using square planar platinum(II) diimine dithiolate complexes containing 4,4'-dicarboxy-2,2'-bipyridine, and 4,7-dicarboxy-1,10-phenanthroline as a diimine ligand. The TiO_2 based solar cell sensitized with platinum(II) complex containing 4,4'-dicarboxy-2,2'-bipyridine and qunoxaline-2,3-dithiolate showed a short-circuit photocurrent of 6.14mA cm^{-2} and open-circuit voltage of 600 mV under simulate AM 1.5 solar irradiation, with an efficiency of 2.6%.

[1] H. Sugihara, L. P. Singh, K. Sayama, H. Arakawa, Md.K. Nazeeruddin, and M. Graetzel, *Chem. Lett.*, **1998**, 1005

Novel aspects of ultrafast electron injection from the excited state of an anchored chromophore to a semiconductor surface

S. Ramakrishna and F. Willig

Hahn-Meitner-Institut, Department SE4, Glienickerstrasse 100, 14109 Berlin, Germany

Recent experimental studies using time-resolved spectroscopy have revealed photo-induced heterogeneous electron transfer to take place in the femtosecond time domain. Moreover, the signals exhibit vibrational coherences which imply that electron injection occurs in the same time-scale as the nuclear vibrational modes, prior to full vibrational relaxation of the donor molecule. In this context two different approaches have been utilized to theoretically model the charge injection as an ultra-fast process:

(A) The density matrix formalism is utilized to model pump-probe spectra of excited state absorption (a three-level problem) and stimulated emission (a two-level problem), when the injecting level is coupled to the empty continuum levels of a finite conduction band of a semiconductor. The calculations show qualitative agreement with experimental results, namely vibronic coherences that are superimposed on temperature independent irreversible charge transfer decays of the excited state as well as the rise of the cationic product state of the molecule. However, it is of utmost interest to explore the effects of reorganizationon on electron transfer which become important when the injecting level is close to the band edge.

(B) A numerical approach has been utilized to obtain the probability distributions in the excited state of the molecule, in the quasi-continuum (QC) of semiconductor electronic states and among the vibronic states of the ionized molecule following excitation of the molecule by a laser pulse of specific central frequency and pulse width. An approximate analytical expression is shown to explain the dependence of the excited state decay on (i) reorganization energy, (ii) energetic position of the the injecting level, and (iii) the initial population profile in the excited vibronic manifold. The spatial location of the excited state vibrational wavepacket is examined to understand the issue of crossing point in heterogeneous charge transfer. The probability distributions in the electronic QC and in the vibronic levels of the ionized molecule display remarkable interrelated structure that can be achieved only via charge injection from a molecule into a solid. Moreover they are amenable to simple laser control. These model calculations can be utilized in understanding ultra-fast photoemission signals which probe electron distributions in the semiconductor as well as vibrational energy distributions of the cation.

Current Transients, Optical Absorbance and Charge Recombination in Dye-Sensitised Nanocrystalline Titanium Dioxide Electrodes

Carol Olson, Richard Willis, Thierry Lutz, James Durrant, and Jenny Nelson

Centre for Electronic Materials and Devices, Imperial College of Science Technology and Medicine, London SW7 2BZ, U.K. Tel: +44 20 7594 7581. FAX: +44 20 7594 7580. E-mail: c.olson@ic.ac.uk.

Understanding the losses associated with electron transport in the titanium dioxide electrodes of dye-sensitised solar cells will enable the optimisation of the electrode for a more efficient solar cell. Charge accumulation in an unsensitised TiO_2 electrode is studied by measuring current transients in response to small potential-step perturbations of a steady-state applied bias. A redox inactive electrolyte is used to suppress interfacial electron transfer. Simultaneous time-resolved measurement of optical absorption at 800 nm indicate the occupation of intra band gap states by injected electrons (Ti^{III} species). In the case of an electrolyte containing 0.1 M $LiClO_4$, analysis of the transient current shows that the dark current is due to two processes: a slow Faradaic diffusion process which may be related to lithium ion intercalation, and a faster capacitive charging of the interface. We show that the optical signal can similarly be resolved into two contributions, one associated with each process, and demonstrate that in each case the absorbance is linearly related to the charge introduced into the TiO_2 film. Extinction coefficients are derived for electrons introduced through the two processes. This relationship enables the quantitative estimation of the density of electrons localised in TiO_2 films from the optical absorbance at 800 nm. We present results for unsensitised TiO_2 electrodes in electrolytes containing different alkali salts in order to clarify the role of Li^+ and other cations.

Recombination between oxidised dye molecules and electrons in sensitised TiO_2 films can be observed by measuring transient absorption following photoexcitation of the dye[1]. We study recombination as a function of applied bias which we relate to injected electron density using values of electron absorbance obtained as described above. By varying the alkali salt in the electrolyte we can observe the effect on both the availability of electrons in the titanium dioxide and their influence on the recombination of the dye cation with electrons in the TiO_2. We discuss the influence of the chemical environment on charge accumulation and recombination in a dye-sensitised solar cell.

---

[1] Yasuhiro Tachibana, Jacques E. Moser, Michael Grätzel, David R. Klug, and James Durrant, J. Phys. Chem., 100, 20056-20062 (1996).

Solid State and Liquid Junction Dye Sensitized Solar Cells: Results using Metal Oxide Bi-Layers

Brian O'Regan, Frank Lenzmann, Francine Duriaux, and Michael Grätzel

Laboratoire de Photonique et Interfaces; Départment de Chemie
Ecole Polytechnique Féderal Lausanne
1015 Lausanne, Switzerland

Knowledge of the electron distribution and motion in nano porous metal oxide films is critical to understanding the operation of dye sensitized liquid junction and solid state solar cells. Results will be presented from porous metal oxide bi-layers of ZnO / TiO_2, Nb_2O_5 / TiO_2, and TiO_2 / SnO_2. In the first two cases only small changes are seen, relative to the single oxide films, whereas in devices where 1 µm films of porous TiO_2 are overlaid with 5 µm films of porous SnO_2, an ~50% reduction in the dye sensitized photocurrent is seen, accompanied by a large reduction in the photovoltage. These results are consistent with a model where the conduction band edges of Nb_2O_5, ZnO, and TiO_2 are very similar (in the electrolytes used) but the SnO_2 conduction band edge is much more positive. The 50% reduction in photocurrent is consistent with a field free diffusion of electrons in the TiO_2 film, or with a symmetric field oriented toward both TiO_2 / SnO_2 junctions. However, as the potential of the SnO_2 substrate can be varied by 500 mV relative to the outer SnO_2 film without changing the ratio of the electrons arriving at each SnO_2 layer, any field in the TiO_2 is clearly not related to the potential of the SnO_2. The large reduction in photovoltage indicates that the recombination of electrons with tri-iodide at the SnO_2 / electrolyte interface is controlling the voltage in these devices, as the voltage is dependent on the SnO_2 surface area.

Additional results will be presented on the dye sensitization of electrodeposited and colloidal ZnO films, incorporated in liquid junction and solid state cells.

Direct Evaluation of Interfacial Reaction Energetics by Time-Resolved Photoacoustic Spectroscopy

Svetlana Leytner* and Joseph T. Hupp
Department of Chemistry, Northwestern University, Evanston, IL 60208 USA

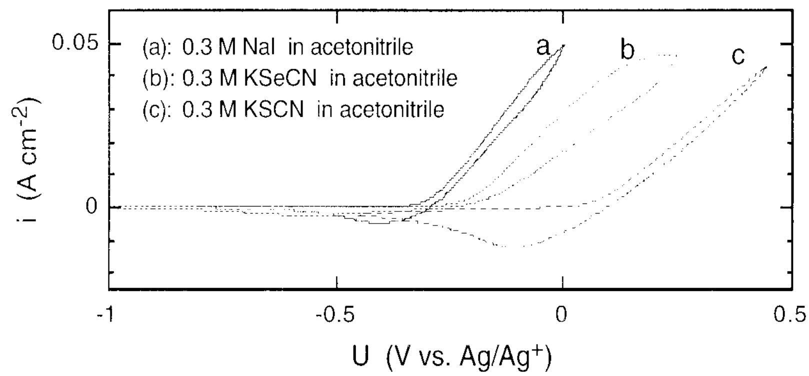
Time-resolved photoacoustic spectroscopy is being employed to study the energetics and kinetics of light-induced electron injection and back electron transfer at dye-functionalized nanocrystalline metal oxide semiconductor/solution interfaces. The technique is based on measuring the heat released into a medium as a result of nonradiative relaxation following absorption of a photon on a nanosecond to microsecond time scale. We demonstrate that this methodology can be utilized to measure the heat release associated with back electron transfer, allowing for direct probing of the semiconductor energy states involved in the electron-transfer process. The experiments were performed in the narrow temperature range of 10-25 °C to distinguish between the reaction volume and enthalpy change contributions to a single acoustic wave. Time resolution was achieved by using deconvolution procedures. We find that back electron transfer from the conduction band can be distinguished from the trap state based electron transfer by time-resolved photoacoustic spectroscopy. In addition, the energetics of photogenerated electrons in nanocrystalline colloidal titanium dioxide dispersed in aqueous solution have been studied. The dominant electron trapping sites were determined to lie 0.8 eV below the conduction band edge.

Influence of the redox couple on the performance of dye-sensitized TiO_2 photoelectrochemical cells

Gerko Oskam[a)], Peter C. Searson[a)], and Gerald J. Meyer[b)]

[a)] Department of Materials Science and Engineering
[b)] Department of Chemistry
The Johns Hopkins University
Baltimore, MD 21218

TiO_2 films sensitized with ruthenium-based dyes have been shown to convert light with an incident photon-to-current efficiency of close to 1, and an energy efficiency of up to 12% has been reported for photoelectrochemical cells. An important factor determining the cell performance is the redox couple in solution. Upon absorption of a photon, the dye injects an electron into the TiO_2 conduction band, and the oxidized dye is reduced by the reducing agent in solution. In order to maximize the energy conversion efficiency the reduction of the dye should involve an as small as possible overpotential, while ensuring a high reduction rate. The reducing agent is then regenerated at the counter electrode, which should also require a minimal overpotential. In addition, the efficiency of regeneration of the dye and the reducing agent strongly affect the life time of the cell. Hence, the equilibrium potential, the exchange current density, the transfer coefficients, and the reversibility of the redox couple are important factors for the performance and life time of dye-sensitized TiO_2 photoelectrochemical cells.



In this paper, we will discuss the electrochemical properties of various redox couples in acetonitrile solutions, and their effect on the cell performance. The Figure shows current – potential curves for 0.3 M solutions of NaI, NaSeCN, and NaSCN in acetonitrile using a platinum disk as working electrode and a $Ag/AgClO_4$ reference electrode. The difference in equilibrium potentials is apparent and the two alternative redox couples have a more positive equilibrium potential than the I^-/I_3^- couple. The Figure also shows that the $SeCN^-$ / $(SeCN)_2$ redox couple is less reversible indicating that a higher overpotential may be needed at high light intensity.

These solutions were subsequently used in dye-sensitized solar cells in a three-electrode configuration, and the IPCE and current-potential curves were recorded as a function of the redox couple. The results will be discussed from both an energetic and kinetic point of view.

Time-resolved photoelectrochemical measurements at electrochemically self-assembled ZnO/dye electrodes

T. Oekermann [1,2] , D.Schlettwein [1] , T. Yoshida [2], T. Sugiura [2] , H. Minoura [2]

[1] Universität Bremen, Institut für Angewandte und Physikalische Chemie,
Postfach 33 04 40, D- 28334 Bremen, GERMANY

[2] Gifu University, Graduate School of Engineering, ERES Division, Yanagido 1-1,
Gifu 501-1193, JAPAN

Dye-sensitization of wide bandgap oxide semiconductors is of considerable interest for applications in solar cells. Recently, we reported about a successful one-step synthesis of dye-modified ZnO thin films by electrodeposition from aqueous mixed solutions of $Zn(NO_3)_2$ and water-soluble dyes, such as metal complexes of tetrasulfophthalocyanines (TSPcMt; Mt = Zn,Al,Si) as well as the xanthene dyes eosin Y and rose bengal [1,2]. The simplicity of the method and a direct crystallization of ZnO without heat treatment are seen as significant advantages. Characterization of the materials has revealed ordered growth of ZnO crystallites and formation of ordered dye assemblies, thus allowing to consider this process as ”electrochemical self-assembly”.

In this study the photoelectrochemical properties of these unique electrochemically self-assembled ZnO/dye thin film electrodes are investigated by measurements of transient photocurrents in the ms-regime and by Intensity Modulated Photocurrent Spectroscopy (IMPS).[3]

The steady-state photocurrents observed at the TSPcMt electrodes can be correlated with the concentration of the dye in the ZnO film. A high dye concentration leads to the formation of dye aggregates. In this case an efficient charge-transfer to the electrolyte is found, leading to low surface charging and low surface recombination of photogenerated holes with electrons from the ZnO. Higher quantum efficiencies are observed in the presence of dye monomers, which are formed at low dye concentrations. These electrodes show more surface charging and recombination of holes but also a much faster electron injection from the dye to the ZnO.[4] This leads to the conclusion that in the case of a high dye concentration a considerable portion of the photogenerated charge carriers already recombine within the dye aggregates, while the holes generated by the dye monomers either are transferred to the electrolyte or they recombine with electrons from ZnO.

When compared to ZnO sensitized by TSPcMt, generally higher photocurrents are observed for ZnO sensitized with xanthene dyes. Those films show a nearly rectangular transient photocurrent response, indicating efficient electron transfer from the dye to ZnO and from the electrolyte to the dye. Extraction of eosin Y by alkaline solutions (more than 90% extracted) leads to a sharp decrease in the steady-state photocurrents, while much higher charging- and discharging currents are observed, indicating slow charge-transfer and considerable recombination. Since eosin Y in the as-deposited film is highly concentrated (0.28 M, assuming homogeneous distribution of dye molecules), efficient hole transfer among neighboring molecules is thereby indicated. This effect enables those dye molecules that are less accessible from the electrolyte to behave as efficient sensitizers also. These molecules remain unextracted and therefore suffer from significant recombination. This special role of the dye layer in the charge transfer process is a unique feature of the electrochemically self-assembled ZnO/xanthene dye films, because this effect was not observed in ZnO/TSPcMt films.

[1] T.Yoshida, K.Miyamoto, N.Hibi, T.Sugiura, H.Minoura, D.Schlettwein, T.Oekermann, G.Schneider, D.Wöhrle, *Chem.Lett*. **7** (1998) 599.

[2] T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, H. Minoura, *Adv.Mater*., submitted

[3] L.M.Peter, *Chem.Rev*. **90** (1990) 753.

[4] D.Schlettwein, T.Oekermann, T.Yoshida, M.Tochimoto, H.Minoura, *J.Electroanal.Chem.* **481** (2000) 42.

Effect of redox solutions on characteristics of dye-sensitized solar cells

Toshihiko Matsuda, Hajime Matsumoto, and Shinji Koike

Department for Energy Conversion, Osaka National Research Institute, AIST
1-8-31 Midorigaoka, Ikeda, Osaka 560-8577, JAPAN

Photovoltaic cells based on dye-sensitized mesoporous TiO_2 films have a great interest as a novel type of solar cell because of their high energy conversion efficiency, exceeding 10%, and low production cost.[1)] The main disadvantage is its dependence on an organic electrolytic solution, which damages its long-term durability.

We have been researching into the dye-sensitized solar cells for the purpose of non-volatilization of the electrolytic solution. As the part of this purpose, here we present the effect of redox solutions on characteristics of the dye-sensitized TiO_2 solar cells.

According to the literature,[1)] dye (cis-Ru(dcbpy)$_2$(NCS)$_2$, Solaronix)-sensitized TiO_2 (P25, Nippon Aerosil) films were prepared on F-doped SnO_2 coated glass plates (Asahi Glass) except for $TiCl_4$ treatment. Pt counter electrodes were prepared by sputtering on glass plates. The dye-coated TiO_2 and the Pt electrodes were fixed together with ionomer resign (Surlyn 1601, DuPont). A small quantity redox solution was introduced between the electrodes, and it was made to be a dye-sensitized solar cell. Electrolytic solutions contained CH_3CN/NMO (50:50 wt%) and 0.3M $(C_4H_9)_4NClO_4$ (TBAP), The concentration of iodine redox was 0.1M $(C_4H_9)_4NI$ (TBAI) and 10mM I_2, ferrocene redox was 0.1M $Fe(C_5H_5)_2$ (Fc) and 10mM $Fe(C_5H_5)_2PF_6$ ($FcPF_6$). A solar simulator (AM1.5, 100mWcm^{-2}) was used as light source. Characteristics of the cells were measured by using a commercial potentiostat, a potential scanner, and a personal computer. Also, three-electrode photoelectrochemical measurements were done. A silver/10mM silver nitrate in CH_3CN containing 0.1M TBAP was used as a reference electrode.

Figure 1 shows characteristics of the solar cells. Dotted and solid lines respectively show iodine and ferrocene redox. In case of the ferrocene redox, either photocurrent or photovoltage hardly generates. Even in the dark (not shown), current flows when voltage was applied. At the applied voltage more negative than –0.6V, cathodic current rapidly increases as well as the iodine redox. This result indicates that the redox reaction of ferrocene on F-doped SnO_2 is dominant, and the TiO_2 films act as a conductor at the applied voltage more negative than –0.6V. Figure 2 shows a linear sweep voltammogram under chopped light illumination for a dye-sensitized TiO_2 electrode in a deaerated 10mM $FcPF_6$ solution without stirring. First, potential was set at -1V vs. Ag/Ag^+, then scanned to 0V at a rate of 20mV/s. Photocurrent responding to the illumination was observed. The flow of photocurrent suggests that Fc works as an electron donor, which exists in a TiO_2 film. With the flow of photocurrent, Fc is oxidized and Fc^+ is produced in the TiO_2 films, and reduction of Fc^+ becomes dominant. That gives rise to a decrease of photocurrent.

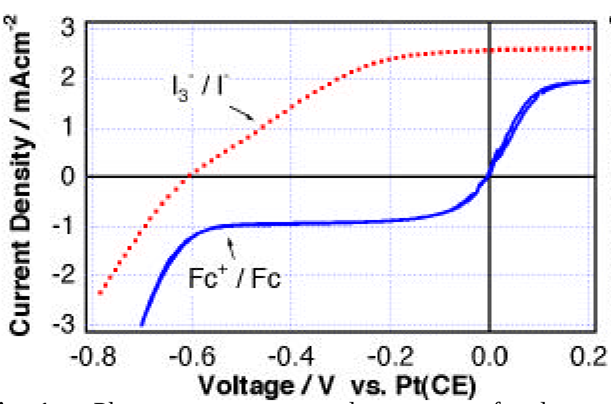


Fig. 1 Photocurrent versus voltage curves for dye-sensitized TiO_2 solar cells in 10mM I_2/0.1M TBAI (dotted line) and 10mM $FcPF_6$/0.1M Fc (solid line) redox solutions. Scan rate: 20mV/s.

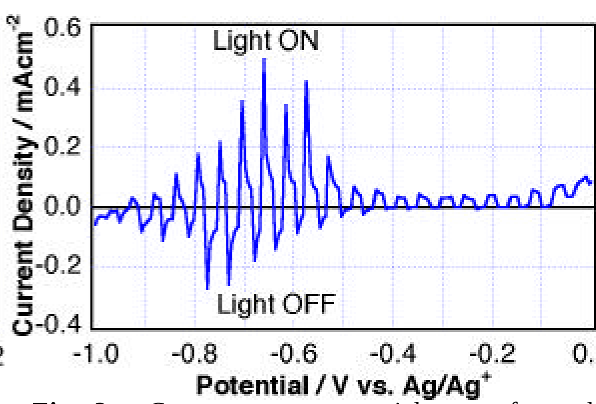


Fig. 2 Current versus potential curve for a dye-sensitized TiO_2 electrode in a 10mM $FcPF_6$ CH_3CN/NMO solution containing 0.3M TBAP under chopped AM1.5 light illumination. Scan rate: 20mV/s.

1) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc.*, **115**, 6382(1993).

The application of extremely low viscose RTMS to the electrolyte for dye sensitized solar cell using EMI fluoride system

Hajime Matsumoto, Toshihiko Matsuda, Shinji Koike
Dept. for Energy Conversion, Osaka National Research Institute, AIST
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Rika Hagiwara, Takayuki Hirashige, Tetsuya Tsuda, Yasuhiko Ito
Dept. of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University,
Sakyo-ku, Kyoto 606-8501, Japan

Room temperature molten salts (RTMS) have been extensively studied for a unique electrolyte for electrochemical devices such as a battery because of its relatively high ionic conductivity, electrochemical stability, and unvolatility. Papageorgiou *et.al.* reported that these unique properties were also valid for long term operation of dye sensitized solar cells (DSC).[1)] However, the short circuit photocurrent (J_{sc}) of the systems was low due to the high viscosity of the using RTMS.

Recently, Hagiwara *et.al.* reported new EMI based RTMS (EMIF-2.3HF) which shows an extremely low viscosity (4.8 cP, 25°C) and high conductivity (120 mS cm^{-1}, 25°C).[2)] We would like to report that the application of EMIF-2.3HF to the DSC system to investigate the effect of viscosity of molten salt on the cell performance.

According to the literature,[3)] dye-sensitized TiO_2 (P25, Nippon Aerosil) films were prepared on F-doped SnO_2 coated glass plates (Asahi Glass) except for $TiCl_4$ post-treatment. Pt counter electrodes were prepared by sputtering on glass plates. The dye-coated TiO_2 and the Pt electrodes were fixed together with ionomer resign (Surlyn 1601, DuPont). Cyclic voltammogram (CV) of EMIF-2.3HF containing 0.06 M NPr_4I and 15 mM I_2 was measured based on the redox potential of iodine/triiodide couple (I^-/I_3^-) contained in EMI-TFSI.

Ammonium iodide, imidazolium iodide and iodine easily dissolved in EMIF-2.3HF. These iodide containing RTMS exhibit multi step anodic current, which was not seen in the absence of iodide. However, cathodic current peak was only one and the potential was near 0 V *vs* I^-/I_3^-. (Fig.1) The fact suggests that iodide containing EMIF-2.3HF can be applied to the electrolyte of DSC system based on N3.

Under the illumination of AM 1.5, DSC cell containing EMIF-2.3HF shows relatively high J_{sc}. The result shows that photo current of DSC depend on the viscosity even in RTMS. If the electrolyte contained a certain amount of additional LiI, much higher J_{sc} would be achieved as in the case of conventional organic solvent. Addition of t-butylpyridine (TBP) increased the open circuit photo voltage, however, decreased the J_{sc} because the viscosity of TBP was higher than that of EMIF-2.3HF.

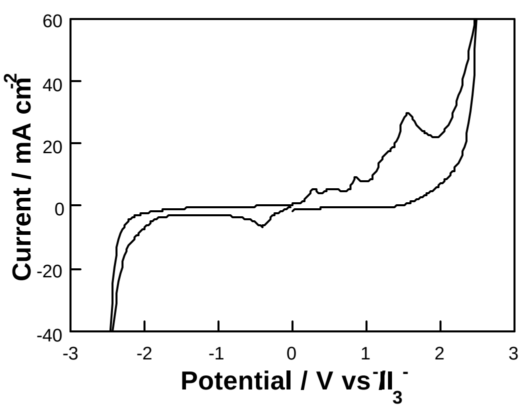


Fig.1 Cyclic voltammogram of EMIF-2.3HF containing 0.06 M NPr_4I, 15 mM I_2. **W.E.**:GC., **C.E.**:Pt, **R.E.**:Pt immersed in EMI-TFSI containing 0.06 M NPr_4I, 15 mM I_2 (T=22°C)

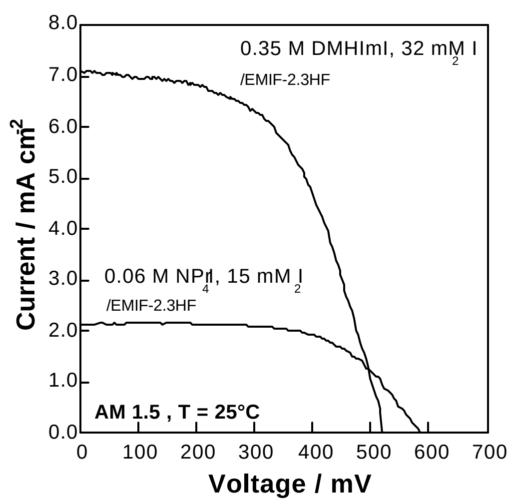


Fig.2 Photocurrent versus voltage curves for dye-sensitized TiO_2 solar cells. Scan rate: 20 mV/s.

References
1) N. Papageorgiou *et al*., *J. Electrochem. Soc.*, **143**, 3099(1996).
2) R. Hagiwara *et al*., *J. Fluorine Chem.*, **99**, 1 (1999).
3) M. K. Nazeeruddin *et al*., *J. Am. Chem. Soc.*, **115**, 6382(1993).

How Porosity Modifies the Photovoltaic Effect in Nanocrystalline Solar Cells

Brian A. Gregg and François Pichot
National Renewable Energy Laboratory
Golden, Colorado 80401-3393

The porosity of the nanocrystalline semiconductor affects many aspects of the photoconversion process in dye-sensitized solar cells, thus distinguishing them mechanistically from conventional photovoltaic and photoelectrochemical cells. We discuss several examples from our recent work: 1) The porosity influences the location and magnitude of equilibrium, photogenerated, and applied electric fields. Thus, photoinduced electric fields are rapidly neutralized, but only if there is excess mobile electrolyte. 2) Because the adsorbed sensitizing dye sits in the electrical double layer, its redox potential is not fixed relative to either the semiconductor or the solution. 3) To distinguish experimentally between two competing models of the photovoltage-determining mechanism in nanoporous solar cells, we deposited dye-sensitized TiO_2 films on four different substrates having vacuum work functions spanning a 1.4 eV range and measured the photovoltage obtained from these films in three different redox electrolyte solutions. No significant differences in photovoltage were obtained on the different substrates, showing that the photovoltage is determined by photoinduced chemical potential gradients, not by equilibrium electric fields. 4) The high surface area of the nanocrystalline film puts severe constraints on the hole conductor, because the hole can only escape recombination with electrons in the TiO_2 if the recombination rate is unusually slow. The conventional hole conductor, I_2/I_3^-, simply has very slow kinetics for reduction and thus allows holes to escape recombination, but some of its other properties are less than ideal. We discuss two strategies for passifying recombination sites in nanocrystalline solar cells in order to facilitate the use of other redox couples, such as those needed for solid state versions of the dye cells.

Dynamics of electron transfer processes for N719 dye-ZnO system.

Christophe Bauer, Emad Mukhtar, Sten-Eric Lindquist, Anders Hagfeldt

Department of Physical Chemistry, Uppsala University,
751 21 Uppsala, Sweden

The dynamics of electron transfer between bis(tetrabutylammonium) cis-di(thiocyanato) bis(2,2'-bypiridine -4-carboxylic acid, 4'-carboxylate)Ruthenium (II) (called N719 dye) and nanocristalline ZnO thin films have been studied by femtosecond pump-probe spectroscopy. For ZnO, protonated Ru-dyes form aggregates due to desorption at Zn surface ions in an acidic medium. The ZnO films have been therefore sensitized with the N719 dye, where two protons from the carboxylic groups are replaced by tetrabutylammonium ions compared to the so called N3 dye, avoiding aggregation. The binding mode for the N719 dye on a ZnO surface seems to be different from N3 dye, since the absorption maximum is not blue shift as observed for the N3 dye. FT-IR spectroscopic data suggest a bidentate binuclear coordination type for the carboxylate groups with the surface zinc cation. By following the rise time formation of the dye cation radical state, the electron injection time was found to be ultrafast, < 150 fs. The back electron transfer time monitored by the recovery of the ground state and the disappearance of the dye cation radical state is strongly non-exponential : 2 ps, 20 ps, 500 ps and likely longer. We believe this behavior arises from the presence of different types of electron surface traps, energetically and spatially distributed. To the best of our knowledge, this is the first measurement of the back electron transfer rate between a dye and ZnO semiconductor.

On the role of the equilibrium dark potential in the dye sensitized electrochemical solar cell

Klaus Schwarzburg, Britta Meißner, and Frank Willig

Hahn-Meitner-Institut, Glienicker Str. 100, 14109 Berlin, Germany
schwarzburg@hmi.de

The dye sensitized electrochemical solar cell shows a photocurrent response that can be reasonably well understood by assuming a diffusive motion of photogenerated screened electrons in the nano-porous TiO_2 film. This finding, confirmed by several research groups, has been linked by some groups to the assumption that a dark equilibrium space charge field is not operative in this solar cell. The observed photovoltage of about 0.7V has been attributed to the change in chemical potential under illumination without offering an explanation for the efficient charge separation process in the cell under e.g. 1 sun illumination. In this context it is particularly important to know how a large photocurrent/photopotential can be sustained uphill against a high photovoltage in the absence of a dark potential. On the other hand, basic laws of thermodynamics require the establishment of a dark electric field of significant strength in the dye sensitized electrochemical solar cell as constructed by the Lausanne group. In contrast to a conventional bulk semiconductor, the nm dimensions of the TiO_2 network and the highly conductive electrolyte confine this equilibrium dark potential to a region of a few nm width close the SnO_2 substrate, and photoinjection of electrons does not change the qualitative scenario /1/. Thus, charge separation is driven by the dark equilibrium electric field in this cell. Of course, this notion is not in conflict with the establishment of a gradient in the chemical potential under illumination in this cell.

In this contribution charge separation is discussed for the cell in the presence and absence of an equilibrium dark potential. Recent experimental results obtained by us and in other groups will be considered. In particular, experimental results and modeling of photocurrent transients in dependence on applied bias will be reported. For the Lausanne type dye sensitized electrochemical solar cell it is confirmed that charge separation occurs due to an equilibrium dark electric field.

/1/ Schwarzburg, K.; Willig, F. *J. Phys. Chem. B*, **103**, 5743 - 5746 (1999)

Trap densities and recombination dynamics in nanocrystalline metal oxide films: a comparison of different film fabrication routes and post-treatments.

Richard Willis[a]*, Carol Olson[a], Thierry Lutz[a], Brian O'Regan[c], Michael Grätzel[c], Paul O'Brien[b], Jenny Nelson[a] and James R. Durrant[a]

[a] Centre for Electronic Materials and Devices, Departments of Physics and Chemistry, Imperial College, London, SW7 2AY , UK
[b] Department of Chemistry, University of Manchester, Manchester, U.K.
[c]Laboratoire de Photonique et Interfaces, Dept. Chemie, Ecole Polytechnique Féderal de Lausanne
1015 Lausanne, Switzerland

*Presenting Author: r.willis@ic.ac.uk

Dye-sensitised photovoltaic devices often employ nanocrystalline metal oxide thin films as their high surface area allows sufficient light to be absorbed by a single monolayer of adsorbed dye. Such nanocrystalline films have a high surface area to volume ratio and have been widely reported to exhibit a high density of trapped states (REFS). It has been suggested that these trapped states strongly influence the electron transfer in the film and it's transport. In previous studies published by our group we have employed transient absorption spectroscopy to investigate the charge recombination kinetics between the dye cations and the electrons in nanocrystalline titanium dioxide films. Specifically, we concluded that the charge recombination kinetics were strongly influenced by the electronic occupancy of the trapped states in the TiO_2.

The ability to link the morphological and electronic properties of the oxide to the rate of charge recombination and, ultimately, the performance of the photovoltaic device would prove very useful in the development of higher efficiency devices. In this poster we extend our previous studies to compare the influence of the electronic traps by varying their density in the films.

We have prepared TiO_2 and ZnO nanocrystalline films from sol-gel based routes. By varying the fabrication route and the sintering conditions we have produced morphologically similar films with different defect densities. A chronoamperometric technique, probing the capacitance of the film, was used to monitor the density of trapped states in each film. Transient absorption studies of the rate of charge recombination at the metal oxide - electrolyte interface have also been undertaken and are presented here. The results presented here are discussed with relevance to the function of the films in dye sensitised solar cells.

Solid state dye sensitised photovoltaic cells employing a polymer electrolyte.

Saif A. Haque*[†], Sven Sodergren[†], Andrew Holmes[‡], Rainer Martin[‡], Ivan Montanari[†] and James R. Durrant[†].

[†]Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College, London SW7 2AY, U.K., and [‡]Melville Laboratory for Polymer Synthesis, Department. of Chemistry, University of Cambridge, UK .
*Presenting Author:s.a.haque@ic.ac.uk

Photoelectrochemical solar cell devices based on dye sensitised nanocrystalline semiconductor materials have attracted considerable interest. This mainly stems from the ability of such devices to convert light to electrical energy with efficiencies as high as 10% [1]. These devices employ cheap materials and extremely simple fabrication techniques. However a major disadvantage of such devices is the necessity of using a liquid based redox electrolyte typically iodide/triiodide in an acetonitrile solvent. A number of difficulties in encapsulation of this liquid electrolyte considerably hinder the long-term stability of these devices. An alternative to the liquid system is to replace it with a solid polymer electrolyte. With this approach it is possible to circumvent the problems associated with leakage and encapsulation of the liquid electrolyte and ultimately enhance the overall stability.

In this paper we present a solid state dye sensitised nanocrystalline solar cell employing an ionic polymer electrolyte. The absence of any liquid solvents allows the fabrication of sandwich cells without any sealing materials. Unsealed devices employing this hole transporting medium exhibit monochromatic incident photon to current conversion efficiencies (IPCE) of > 30%. Under 1/10 AM 1.5 illumination such devices achieve a photocurrent of 0.4 mA and an open circuit voltage of -400 mV, which correspond to an overall cell efficiency of 1.5%.

Interfacial electron transfer kinetics are critical to the efficiency of dye sensitised photovoltaic devices. In previous work from our laboratory we have employed transient absorption spectroscopy to study the electron transfer kinetics at the semiconductor/dye/liquid electrolyte interface [2]. In this paper we extend these studies to investigate the kinetics at the semiconductor/dye/ionic polymer electrolyte interface.

Nature. 1991, *353*, 737-739.
[2] Haque, S.A., Tachibana, Y., Willis R.L., Moser, J.E., Grätzel, M., Klug, D.R. and Durrant, J.R. *J. Phys. Chem. B* 2000, 104, 538-547.

Competition between charge recombination and dye re-reduction from the electrolyte in nanocrystalline dye-sensitised TiO_2 electrodes.

Ivan Montanari*, Jenny Nelson, David R. Klug, James R. Durrant

Centre for Electronic Materials and Devices , Departments of Chemistry and Physics, Imperial College, London SW7 2AY, Great Britain

*Presenting author: Fax: 44-171-5945806, e-mail: i.montanari@ic.ac.uk

Dye-sensitisation of wide bandgap semiconductors has been succesfully utilised in photoelectrochemical cells for a number of years[1]. A detailed understanding of the kinetics involved in the functioning of such cells is both scientifically interesting *per se* and important in technological development of such devices. Previous studies have established the ultrafast nature of electron injection[2] and looked at the strongly bias dependent recombination kinetics[3]. In this paper we extend these studies to the events following ultrafast injection, namely kinetic competition between charge recombination from the semiconductor film and electron transfer from I^- ions in solution to rereduce the dye cation. The kinetics of the rereduction reaction have in particular received little attention to date, although it has been suggested that a slow rate of this reaction is responsible for the poor performance in Os(bpy)2(dcb)–sensitised cells[4].

Transient absorption spectroscopy was employed to monitor the decay of absorption of the dye cation as its concentration is depleted by the two competing processes. Data were collected as a function of iodide concentration and applied electrical bias. The iodide reaction was found to be strongly dependent upon iodide concentration but independent of the bias applied. The effect of externally applied bias on this branching ratio has been assessed. The number of electrons in the film measured spectroelectrochemically at different external biases is correlated with the kinetics observed. Work is in progress to develop a model to predict the outcome of this kinetic competition in functioning photoelectrochemical devices.

References

1) O'Reagan & Grätzel *Nature* (1991), 353, 737-739
2) Tachibana et al. *J. Phys. Chem.* (1996), 100, 20056-20062
3) Haque et al. *J. Phys. Chem. B* (1998), 102, 1745-1749
4) Alebbi et al. *J. Phys. Chem. B* (1998), 102, 7577-7581

Electronic Energy Levels of Dye-Sensitized TiO_2 Determined with Photoelectron Spectroscopy

Sven Södergren[1,3], Karin Westermark[1], Anders Henningsson[1], Håkan Rensmo[2], Anders Hagfeldt[2] and Hans Siegbahn[1]

[1] Department of Physics, Box 530, S-751 21 Uppsala, Sweden,

[2] Department of Physical Chemistry, Box 532, S-751 21 Uppsala, Sweden,

[3] Chemistry Department, Imperial College, SW7 2AZ London, UK.

The electronic energy levels in the Grätzel cell have been determined by photoelectron spectroscopy, PES. By combining measurements of a blank, a lithium intercalated and a dye-sensitized TiO_2 electrode, a picture of the energy levels was constructed (figure 1). Whereas the occupied energy levels are probed directly in a PES measurement, the positions of the conduction band and the excited states of the dye were determined by using the optical absorption of the materials*. Bandgap states were observed all the way up to the conduction band as a result of lithium intercalation. In particular at 2.1 eV above the valence band edge a pronounced peak appears in the density of states. The excited states of the dye were found to overlap with the lowest part of the conduction band of TiO_2.

The presence of these local trap states, induced by small cations, will be discussed as important factors influencing the solar cell output.

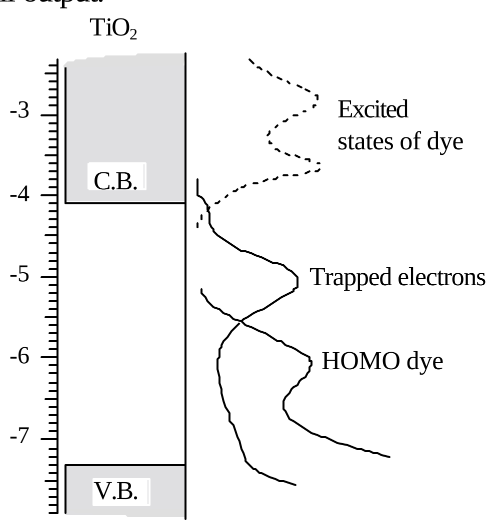


Figure 1. The energy levels of the Grätzel cell, as determined by photoelectron spectroscopy. Accuracy meV. The electronic relaxation for TiO_2 and dye were assumed to be equal in the photoemission process.

* 3.2 eV for the TiO_2 bandgap (anatase) and 2.35 eV for the maximum absorption of the dye, $Ru(dcbpy)_2(NCS)_2$, "N3".

Investigation on femtosecond dynamics of $Ru(dcbpy)_2(SCN)_2$ excited state and the dye cation on TiO_2 films

J. Kallioinen, J. Korppi-Tommola, V. Lehtovuori and P. Myllyperkiö

University of Jyväskylä, Department of Chemistry,
P.O. Box 35, FIN-40351 Jyväskylä, Finland

Photophysics of Ru(2,2'-bipyridyl-4,4'-dicarboxylate)$_2$(SCN)$_2$ sensitized nanocrystalline TiO_2 films were studied by femtosecond transient absorption spectroscopy in the wavelength region 700-900 nm. In this area signal of the dye sensitized TiO_2 films arise from the dye cation, injected electrons and free dye. Therefore dye sensitized Al_2O_3 films and ethanol solutions were used as a reference to clarify the contribution from excited state absorption on the observed signals.

It has been reported that electron injection and formation of ^{3}MLCT state occur faster than 100 fs.[1,2] Also a small picosecond component has been observed, but the origin of this component is unclear.[2,3] Our main interest was to study the long rise time (>1ps) kinetics in the dye sensitized TiO_2 films after fast electron injection. It was observed that rise times and corresponding amplitudes are both wavelength and site dependent. In dye sensitized Al_2O_3 films where no electron injection is expected no such behaviour was observed. By analyzing the amplitudes of the rise time components in different samples, we suggest that the long rise time (>ps) is due to slow electron transfer from ^{3}MLCT to TiO_2.

References:

1. Ellingson R.J., Asbury J.B., Ferrere S., Ghosh H.N., Sprague J.R., Lian T. and Nozik A.J., *J.Phys.Chem.B*, 1998, **102**, 6455-6458.
2. Asbury J. B., Ellingson R. J., Ghosh H. N., Ferrere S., Nozik A.J. and Lian T., *J.Phys.Chem.B*, 1999, **103**, 3110-3119.
3. Tachibana Y., Moser J.E., Grätzel M., Klug D.R. and Durrant J.R., *J.Phys.Chem.*, 1996, **100**, 20056-20062.

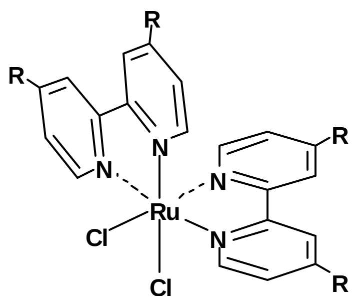
Semiempirical Configuration Interaction Calculations of the Absorption Spectra of Some 2,2'-bipyridine Containing Ru(II) Compounds

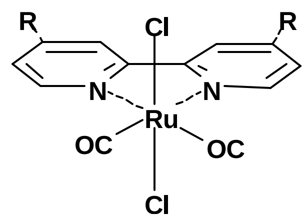
J. Kallioinen*, J. Korppi-Tommola*, M. Haukka, S. Luukkanen and T.A. Pakkanen

**University of Jyväskylä, Department of Chemistry*
P.O.Box 35, FIN-40351 Jyväskylä, Finland

University of Joensuu, Department of Chemistry,
P.O.Box 111, FIN-80101 Joensuu, Finland

Chemical compounds that absorb sun's light efficiently and are suitable for use in dye sensitized solar cells are under intensive development. Many organometallic ruthenium dyes have been syntetized and tested in dye sensitized solar cells and about 10% efficiencies have been reported.[1] We have used a computational approach to find out how well light absorption properties of some 2,2'-bipyridine containing ruthenium(II) dyes can be predicted. Our main interest was to study substitution effects of the 2,2'-bipyridine with $-CH_3$, $-NO_2$ and -COOH groups at 4,4' position.





Absorption spectra were calculated by using intermediate neglect of differential overlap method parametrized for spectroscopy at configuration interaction (CI) level of theory (ZINDO/S). All starting geometry optimizations were carried out by a non-local hybrid density functional method B3PW91, as incorporated in the Gaussian 94 and Gaussian 98 program packages. A standard double zeta basis set 6-31G* was used for all other elements except ruthenium. For ruthenium, Huzinaga's extra basis was used. Geometries refer for the complexes in gas phase and no solvent interactions were taken into account. The computed vacuum values were systematically blue shifted with respect to the experimental spectra. Nevertheless computed transitions for different substitutions follow well the trends observed in the experimental spectra.

[1]B. O'Regan and M. Grätzel, *Nature*, **353**, 737, (1991).

Calculated dye-surface interactions in dye-sensitized solar cells

P. Persson*, R. Bergström, and S. Lunell

Department of Quantum Chemistry, Uppsala University, Box 518, S-751 29 Uppsala, Sweden

The binding of dyes to TiO_2 nanocrystals, and the electronic interactions at these interfaces, are central issues for a molecular level understanding of dye-sensitized solar cells. We present results from quantum chemical calculations of sensitized TiO_2 nanocrystals, which address both these questions.

Bi-isonicotinic acid (2,2'-bipyridine-4,4'-dicarboxylic acid) is the anchoring ligand in many ruthenium dyes (e.g. N3), and we have compared different binding possibilities of this ligand to important TiO_2 surfaces, such as anatase (101). The calculations show the importance of structural deformations to accommodate strong surface binding.

The surface electron transfer in dye-sensitized solar cells is believed to occur from an excited state of the sensitizer, to the TiO_2 conduction band. Our calculations indicate that a low-energy peak in the absorption spectrum of catechol sensitized TiO_2 is instead due to a direct photo injection of a catechol ground-state electron to the TiO_2 conduction band, with no involvement from excited states of the sensitizer.

The electronic coupling strength between sensitizer excited states and the TiO_2 conduction band is often a crucial parameter for the surface electron transfer rate. Calculations on different sensitizers shows that the coupling strength varies from weak (meV) to strong (eV) depending on the sensitizer, the nature of the excited state, and the position of the excited state relative to the TiO_2 conduction band. Furthermore, the calculations indicate that the binding to the TiO_2 causes important changes to the excited states of the sensitizers.

In short, we have found that semiempirical and first principles quantum chemical calculations, on nanometer sized clusters and periodic surfaces, can provide a molecular level understanding for many of the complex interactions in dye-sensitized solar cells.

Cations, Protons, and Deuterons at Photosensitized Titanium Dioxide Nanocrystalline Surfaces

Ping Qu and Gerald J. Meyer
Department of Chemistry, the Johns Hopkins University, Baltimore, MD 21218

Photosensitized titanium dioxide nanocrystalline films have drawn wide attentions since Grätzel and coworker's pioneering work. The transparent nature of these films provide convenient use of transmittance based spectroscopic methods to characterize the photodriven electron transfer processes. Previously we demonstrated the effects of cations such as Li^+ and Na^+ on the interfacial electron injection quantum yield.[1] Here we expand upon this previous work by treating TiO_2 and ZrO_2 colloidal films with acidic or basic aqueous solutions prior to sensitizer binding. The preliminary results show that by controlling the surface acid-base properties, the sensitized materials display dramatically different spectroscopic as well as electrochemical behavior. Figure 1 shows the absorption spectra of $Ru((4,4'\text{-}CO_2Et)_2\text{-bpy})(bpy)_2^{2+}$ bound to pretreated TiO_2 surfaces. Sensitizer attached to base pretreated metal oxide films resembles $Ru((4,4'\text{-}CO_2^-)_2\text{-bpy})(bpy)_2$, while the acid treated samples are well described by $Ru(4,4'\text{-}(CO_2H)_2\text{-bpy})(bpy)_2^{2+}$. Surface binding was also characterized by FTIR. The presence of surface protons greatly enhanced the incident photon-to-current-conversion-efficiency (IPCE), Figure 2. Sensitizers attached to base pretreated TiO_2 films display negligible IPCE with tetrabutylammonium iodide/iodine as the redox active electrolyte. Employment of lithium iodide/iodine effectively increases the IPCE of and base pretreated films. Quantum yields for electron injection, determined by comparative actinometry, provide similar results. Further experiments such as replacing protons with deuterons are presently being carried out. The results demonstrate how judicious selection of electrolytes or surface treatment can affect the fate of excited sensitizers on TiO_2 surfaces.

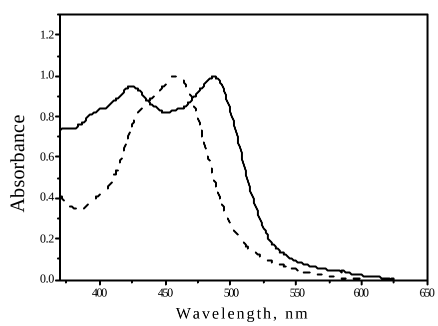


Figure 1. Absorption spectra of $Ru((CO_2Et)_2\text{-bpy})(bpy)_2^{2+}$ on acid (solid) and base (dash) pretreated TiO_2 surfaces. The spectra on ZrO_2 surfaces are the same within experimental error.

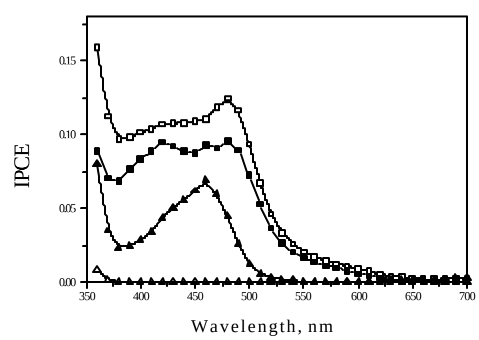


Figure 2. IPCE of $Ru((CO_2Et)_2\text{-bpy})(bpy)_2^{2+}$ on acid (square) or base (triangle) pretreated TiO_2 films with tetrabutylammonium iodide/iodine (solid) or lithium iodide/iodine (open) in acetonitrile.

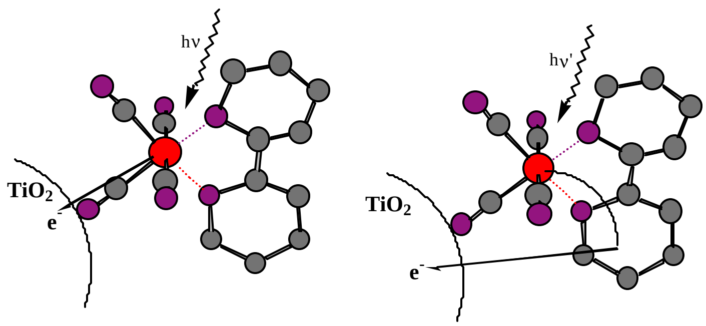
[1] Kelly, C. A.; Farzad, F.; Thompson, D. W.; Stipkala, J. M.; Meyer, G. J. *Langmuir* **1999**, 20, 7047-7054.

TiO_2 Sensitization from the Ground- and Excited-States of $Na_2[Fe(bpy)(CN)_4]$

Mei Yang, David Thompson, and Gerald J. Meyer
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

Semiconductor sensitization is an attractive approach for the conversion of light-into-electricity. Visible light sensitization of n-type semiconductors has been accomplished by electron transfer from either the excited or the ground state to the semiconductor. Here we report the first example of a molecular compound designed to sensitize semiconductors to visible light by electron transfer from *both* ground and excited states.

The compound is $Na_2[Fe(bpy)(CN)_4]$, where bpy is 2,2'-bipyridine. About ten years ago it was shown that metal cyanides, such as ferrocyanide, $Fe(CN)_6^{4-}$, bind to TiO_2 through ambidentate cyano ligands and M $\rightarrow$ Ti(IV) intervalence charge transfer bands appear in the visible region. More recently, sensitization of the same semiconductor by the metal-to-ligand charge transfer (MLCT) excited states of Fe(II) polypyridyl



Ground State Sensitization **Excited State Sensitizatio**

compounds was realized. By combining both ground and excited state electron transfer into one molecular compound as shown schematically above, broad spectral semiconductor sensitization may be realized for solar energy conversion applications. Since the two charge transfer pathways have distinct dynamics and efficiencies, the resultant sensitized material will display time-dependent optoelectronic responses that can be controlled by surface properties and fine tuned at the molecular level for other applications. For example, we find that in neat acetonitrile the injection yield from $[Fe(CN)_4bpy]^{2-}/TiO_2$ is low. The addition of $LiClO_4$ to the acetonitrile bath increases the injection yield. Our preliminary interpretation is that the excited state injection yield can be tuned by the ionic strength while the ground state injection can not. The dynamics of electron transfer and the photoelectrochemical properties of this and closely related compounds will be presented.

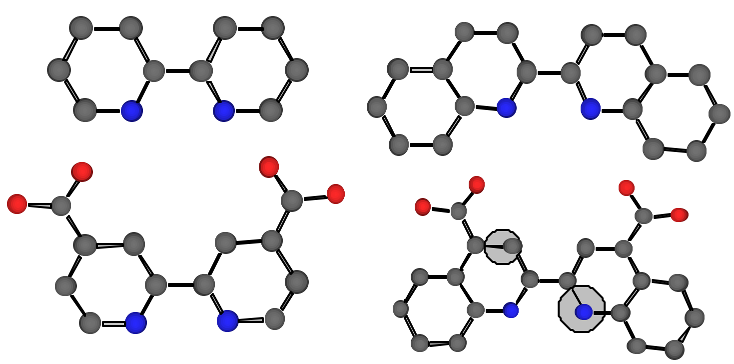
Tuning Light to Electrical Energy Conversion Efficiencies with Heteroleptic Coordination Compounds

Paul G. Hoertz, David Thompson, and Gerald J. Meyer

Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218

The quest for new materials and compounds that efficiently harvest solar energy continues to be an important goal. An attractive approach has been to utilize wide bandgap semiconductors sensitized with inorganic coordination compounds in regenerative solar cells. Light-to-electrical energy conversion efficiencies realized in these devices are remarkably high and can approach unity at individual wavelengths of light. This technology, therefore may represent the first time in which devices that operates on a molecular level are competitive with traditional solid state photovoltaics.

An important issue that has recently been raised concerns the rate of electron transfer from the sensitizer excited state(s) to the semiconductor. Ultrafast absorption measurements performed in vacuum have revealed femtosecond injection rates, leading to some speculation that interfacial electron transfer occurs from the Frank–Condon state. To address this issue, we report photoelectrochemical and photophysical studies on a series of four heteroleptic Ru(II) compounds (based on 2,2'-bipyridine and 2,2'-biquinoline ligands, shown below) anchored to nanocrystalline TiO_2 electrodes. The absorption spectrum of these compounds reveal well-resolved metal-to-ligand



charge transfer (MLCT) bands. For example, in $[Ru(bpy)_2deebq]^{2+}$ (where deebq is 4,4'-diethylester-2,2'-biquinoline), the high energy band, λ_{abs} ~ 450 nm, is assigned to Ru(II) → bipyridine charge transfer while the lower energy band is assigned to Ru(II) → biquinoline charge transfer, λ_{abs} ~ 550 nm. UV-Vis absorption, emission, and photocurrent measurements after selective excitation into these bands allows unambiguous identification of the molecular excited state(s) involved in interfacial electron transfer. Based on this data, the heteroleptic compounds allow us to also address the importance of having the thermally equilibrated excited state localized on a ligand adjacent to or remote from the semiconductor surface. Furthermore, these sensitized materials provide an opportunity to probe 'hot' interfacial electron transfer processes on a molecular level.

Solvatochromism of $TBA_2[Ru(dcb)(CN)_4]$ bound to Titanium Dioxide Surfaces

Georg M. Hasselmann[§], Carlo A. Bignozzi[£], Roberto Argazzi[£], and Gerald J. Meyer[§]

[§]The Johns Hopkins University Baltimore, MD 21218
[£]Dipartimento di Chimica dell'Università, Centro di Studio
su Fotoreattività e Catalisi CNR 44100 Ferrara, Italy

$Ru(dcb)(CN)_4^{2-}$ (**1**), where dcb is 4,4'-(CO_2H)-2,2'-bipyridine, was bound to nanocrystalline (anatase) TiO_2 and its photophysical and electrochemical properties were studies in a variety of solvents. The parent compound, $Ru(bpy)(CN)_4^{2-}$ (**2**), has recently been reported in the literature[1,2]. This coordination compound is solvatochromatic and will serve as an excellent sensitizer for probing solvent effects at semiconductor electrolyte interfaces. The solvatochromic properties of this compound are pronounced and have been modeled extensively in fluid solution[2]. The complex is yellow in water and deep blue in dimethylformamide, for example. To a first approximation the color changes result from a highly solvent dependent metal based reduction potential presumably due to donor-acceptor interactions with the cyano ligands. The excited sensitizer is a potent reductant and efficiently injects electrons into TiO_2. Surface bound **1** affords the unique opportunity to systematically probe the thermodynamic driving force for charge recombination by changing the solvent. It also allows for spectroscopic studies with solvents in which **2** is insoluble. Simply placing a $Ru(dcb)(CN)_4^{2-}/TiO_2$ colloidal film in different solvents and measuring the absorption spectrum and reduction potential allows us ascertain how well solvated the surface bound sensitizer is. In principle, **1** may bind to TiO_2 through either the ambidentate cyano ligands [3] or through one or both of the carboxylic acid groups. To separate contributions from the TiO_2 side of the interface, $Ru(dcb)(bpy)_2^{2+}$ was explored under the same conditions. $Ru(dcb)(bpy)_2^{2+}$ is weakly solvatochromic and the $Ru^{III/II}$ potential does not shift significantly with solvent. A comparison of the photophysical properties of these two assemblies sheds light on the driving force dependence and reorganizational energy that accompany interfacial electron transfer.

References:

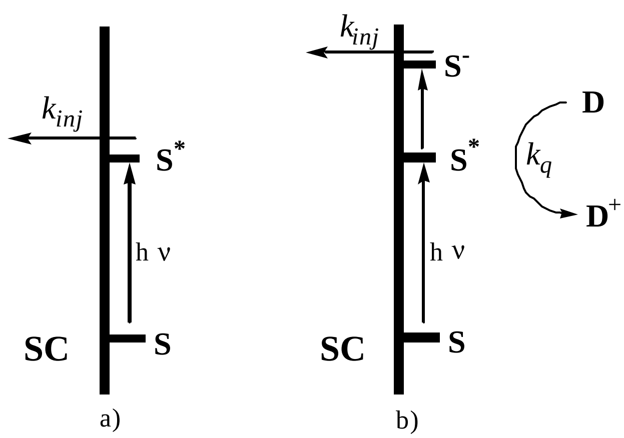
[1] C.A. Bignozzi, C. Chiroboli, M.T. Indelli, M.A.R. Scandola, G. Varani, and F. Scandola "A Simple Poly(pyridine)ruthenium(II) Photosensitizer: (2,2'-Bipyridine)tetracyanoruthenate(II)", *J. Am. Chem. Soc.* **1986**, *108*, 7872.
[2] C.J. Timpson, C.A. Bignozzi, B.P. Sullivan, E.M. Kober, and T.J. Meyer "Influence of Solvent on the Spectroscopic Properties of Cyano Complexes of Ruthenium(II)", *J. Phys. Chem.* **1996**, *100*, 2915.
[3] E. Vrachnou, M. Grätzel, and A.J. McEvoy "Efficient Visible Light Photoresponse Following Surface Complexation of Titanium Dioxide with Transition Metal Cyanides", *J. Electroanal. Chem.* **1989**, *258*, 193.

Reductive Quenching of Molecular Excited States on Wide Bandgap Semiconductor Surfaces

Bryan V. Bergeron, David Thompson, and Gerald J. Meyer

Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218

An attractive approach for solar energy conversion has been to utilize wide bandgap semiconductors sensitized with inorganic coordination compounds in regenerative solar cells. In the commonly accepted model for dye sensitization, the sensitizer excited state(s) transfer an electron to the semiconductor and is then subsequently reduced by an external electron donor present in the electrolyte, Scheme Ia. Here we present spectroscopic and photoelectrochemical data that demonstrate a previously unobserved, alternative mechanism for dye sensitization of colloidal anatase TiO_2, Scheme Ib. In this mechanism, the sensitizer excited state(s) are first quenched by an external donor, D, and subsequently transfers an electron across the interface.



Scheme I

Two particularly important aspects of solar cell operation are the open circuit voltage and short circuit current, V_{oc}, and i_{sc} respectively. The reductive quenching mechanism affords the real possibility of broad spectral sensitization with increased V_{oc} while maintaining a high i_{sc}. Therefore, this alternative mechanism for interfacial electron transfer may be a useful way of improving the power output of regenerative solar cells based on dye sensitization. Through careful choice of electrolyte, donor, and sensitizer we have constructed photoelectrochemical cells that operate by this alternative mechanism. The advantages, disadvantages, and solar conversion efficiencies realized with this approach will be discussed.

Charge Recombination in Sensitized Nanocrystalline TiO_2 Solar Cells

Darius Kuciauskas and Nathan S. Lewis

Division of Chemistry and Chemical Engineering
MC 127-72, California Institute of Technology
Pasadena, CA 91125

Liquid junction solar cells based on sensitized nanocrystalline wide band gap semiconductors have achieved remarkable efficiencies. However, photo- and electrochemical processes taking place in these devices are incompletely understood. To this end, we have used optical spectroscopy to study charge recombination in solar cells sensitized by Ru and Os bipyridyl complexes $Ru(H_2L')_2(CN)_2$, $Os(H_2L')_2(CN)_2$, $RuL'_2(NCS)_2$, $Os(H_2L')_2(NCS)_2$, and $Os(H_2L')_2Cl_2$. (L' is 4,4'-$(CO_2H)_2$-2,2'-bipyridene).
Nanocrystalline TiO_2 films on SnO_2:F conductive glass substrates were obtained from INAP (Germany). Ru and Os compounds were synthesized as previously described. The electrolyte was 0.5 M LiI/0.04 M I_2 or 0.5 M $LiClO_4$ in acetonitrile, to which 0.02 M pyridine and pyridine triflate were added to control proton activity and to ensure stability of the cell.
Ru and Os complexes in this series have similar excited state oxidation potentials, but their ground state oxidation potentials differ by about 0.7V, which allowed us to probe the dependence of the interfacial charge recombination on the driving force. Osmium polypyridyl complexes have more negative ground state reduction potentials, and therefore their absorption spectra are red shifted, making Os complexes, especially $Os(H_2L')_2(CN)_2$, promising sensitizers.
Consistent with previous studies, we have found that charge recombination occurs on micro- to millisecond time scales. From measurements at different excitation intensities we determined that observed transients could be satisfactory described with second order equal concentration kinetics.
We find that for the series of sensitizers investigated, charge recombination occurs in the Marcus inverted region. Studying temperature dependence on charge recombination allowed us to estimate electronic coupling and reorganization energies. We find that from –10°C to +80°C charge recombination rate constants are temperature dependent. Temperature data was well-described by the classical Marcus expression, but not by the semi-classical (Jortner) formula. Electronic couplings estimated from data fits are ~10 to 100 cm^{-1}, and reorganization energies are 0.5 to 0.8eV for this series of complexes.
In addition, charge recombination rate constants exponentially depend on the applied potential. At more positive applied potentials, charge recombination rate becomes independent of the potential, suggesting that TiO_2 trap states mediate recombination reactions under these conditions.
When the ground state oxidation potential of the bipyridyl sensitizer is more positive than about 0.4V, oxidized metal(III) complexes are regenerated by I^- on a much faster time scale than the charge recombination reaction. For complexes with the ground state reduction potentials more negative than 0.4V, the cell efficiency appears to be limited by sensitizer regeneration.

Title: The Use of Adsorbed Blocking Layers to Prevent Electron Transfer Between TiO_2 and I^-/I^{3-} in Nanocrystalline Solar Cells.

Authors: Elizabeth Mayo — California Institute of Technology
Darius Kuciauskas — California Institute of Technology
Genevieve Sauve — Bell Atlantic Laboratories

Nathan S. Lewis* — Division of Chemistry and Chemical Engineering
127-72
California Institute of Technology
Pasadena, CA 91125

Abstract: Dye sensitized nanocrystalline TiO_2 solar cells show great promise as a cost-efficient means of converting light to electricity with overall efficiencies exceeding 10%. This self-regenerative cell is based on excitation of a Ruthenium or Osmium based dye followed by injection into the conduction band of TiO_2. Back reaction of the injected electron with the redox couple in solution is a significant source of efficiency loss. Adsorption of blocking layers onto the TiO_2 surface to prevent this interaction shows great promise as a means of hindering this back reaction and thus allowing for greater efficiencies and the possibility of using other redox couples in such systems for improved overall system performance.

ALL SOLID-STATE SELF-POWERED ELECTROCHROMIC WINDOW WITH PMMA GEL ELECTROLYTE

Lianyong Su
Institute für Physikalische Chemie, Universität Freiburg , Stefan-Meier Straße 21, D-79104 Freiburg, Germany (suliang@fmf.uni-freiburg.de)

Intensified research efforts to develop electrochromic devices have spread worldwide in recent years The focus of these research programs is on large area window applications. For such applications, all solid state electrochromic devices have unique advantages(such as reliability and safety) when compared to conventional liquid-based devices. Although electrochromic windows can be employed to provide user control of light transmission, such devices require an externally applied voltage to control the electrochromic behavior of the device. The requirement for wiring every window into the building´s electrical mains adds significantly to the production cost, particularly if the electrochromic window is being retrofit into an existing building. By incorporating a photovoltaic power source into the electrochromic window, however, this wiring cost could be reduced or eliminated, and the installation of the electrochromic window could be greatly simplified. S. Deb et al. has successfully demonstrated that a wide-bandgap, amorphous SiC alloy photovoltaic cell can be monolithically integrated with a Li-doped WO_3 electrochromic device to fabricate a self-powered electrochromic window. Unfortunately, electric short circuits are a serious problem and it has proved difficult to demonstrate a large area device. Solar cells based on dye sensitized mesoporous films of titanium dioxide are low cost alternative to conventional solid state photovoltaic devices. B. A. Gregg et al. illustrates that a dye sensitized photovoltaic cell can be monolithically integrated with a WO_3 electrochromic device to fabricate a new self-powered electrochromic window, which are easily assembled without electrical short circuits. In previous papers, we described the photovoltaic behaviors of dye sensitized TiO_2 microporous electrodes and fabrication of an all solid-state electrochromic smart window with polymer gel electrolyte with high conductivity(1 mS/cm) at room temperature. A combination of a dye-sensitized TiO_2 solar cell, a PMMA gel electrolyte and a WO_3 electrochromic film to produce a novel solid-state self-powered electrochromic window will be demonstrated here. The photoelectrochromic window has been excellent for chromism and memory characteristics.

Reference

1. S. H. Lee, W. Gao, C. E. Tracy, H. M. Branz, S. Deb, J. Electrochem. Soc., 145(1998)3545
2. C. Bechinger, S. Ferrere, A. Zaban, J. Sprague, B. A. Gregg, Nature, 383(1996)608

Nanoporous ZnO Electrodes for Solar Cell Applications

Karin Keis, Sten-Eric Lindquist, Anders Hagfeldt

Uppsala University, Department of Physical Chemistry, Box 532, S-751 21 Uppsala, Sweden.

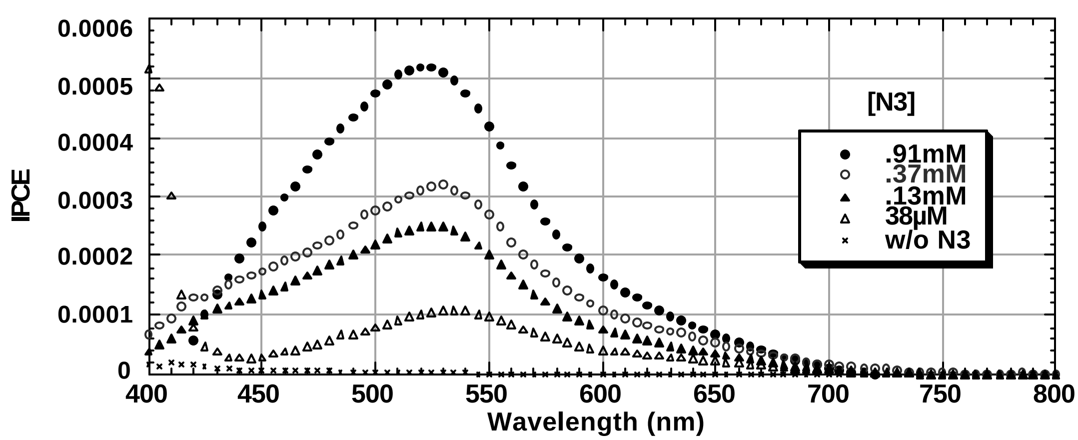
Dye-sensitized solar cells based on nanostructured TiO_2 electrodes are today by far the most investigated and the most efficient ones. From a fundamental viewpoint the ZnO bandgap energy of 3.2 eV and the position of the band edges are very similar to TiO_2, which makes a comparison between the two materials interesting. In our laboratory a thorough optimization of photoelectrochemical solar cells based on nanostructured ZnO with respect to particle size, doping, film thickness, morphology and dye-adsorption has been performed.

Nanostructured ZnO electrodes with one order of magnitude larger spherical particles (150 nm) than normally used in these systems have been found to show high incident photon-to-current conversion efficiencies (90% at 360 nm). No effect on the photocurrent of electron scavengers like iodine and oxygen added to the solution were observed. However, overall efficiencies of the dye-sensitized photoelectrochemical solar cells based on these ZnO electrodes were found relatively low (2 %) compared with cells based on TiO_2. Results from IPCE measurements and IR- and Raman spectroscopies gave evidence of dye agglomeration in nanoporous ZnO films. By avoiding the dye agglomeration in the nanoporous film and improving the interaction between dye and ZnO particles in the film, the overall solar-to-electric energy conversion efficiency was improved by at least a factor of two. Efficiencies of up to 5 % have now been obtained.

Comparison of the Sensitization Behavior of the Anatase and Rutile Crystal Forms of TiO_2 with Various Sensitizers

Akiko Fillinger, Brian France, Norihiko Takeda, Paul Schroeder and Bruce A. Parkinson
Department of Chemistry
Colorado State University
Fort Collins, CO 80523-1872, USA

The success of the Grätzel solar cell has produced a renewed interest in the sensitization of metal oxides. Despite the high efficiencies achieved in the nanocrystalline oxide solar cells there is relatively little known about the details of the binding and organization of dye molecules on the surface of the metal oxides. We have been using oriented anatase and rutile crystals to study the binding of sensitizing dyes to various low-index crystal surfaces. We have used natural anatase crystals for our studies due to the difficulty of growing large crystals of the low temperature form of TiO_2. We compare the adsorption isotherms of various carboxylate-bound sensitizers including ruthenium based (see figure) and perylene based molecules. The quantum yields for electron injection are determined as a function of wavelength for both incident and absorbed photons (see Figure) and comparisons between the different crystal forms and faces are made. Ultra high vacuum (UHV) techniques such as XPS and Auger spectroscopy are used to prepare and characterize the crystals before and after sensitization experiments. Scanning probe microscopies were used to examine the adsorption sites and the organization of the dye molecules on the metal oxide surfaces.



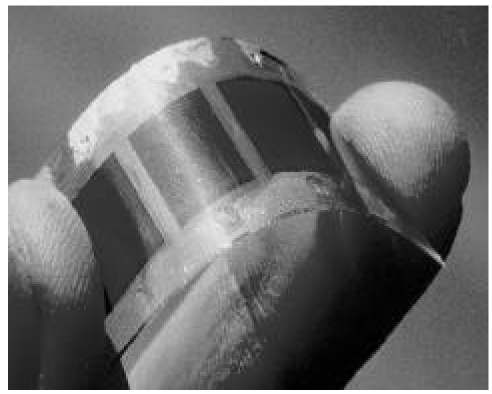
Spectral sensitization of a natural crystal of anatase from Norway treated with various concentrations of the ruthenium-based N3 dye.

Flexible Dye-Sensitized Nanocrystalline TiO_2 Solar Cells

P.M. (Paul) Sommeling, Martin Späth, Jan Kroon, and John van Roosmalen
ECN Solar & Wind, P.O. Box 1, 1755 ZG Petten, The Netherlands,
tel. +31 224 564276, fax. +31 224 563214, email: sommeling@ecn.nl.

The dye-sensitized nanocrystalline TiO_2 solar cell (nc-DSC) developed by Grätzel [1] has the potential to reach low costs in future outdoor power applications. In addition, due to its expected ease of production and possibilities to adjust its appearance, the potential for application is very broad. With respect to the rigid (glass) version, the flexible version can add roll-to-roll production and it is light-weight, non-breakable and easy to integrate [2].

In the development of the flexible dye-sensitized nanocrystalline TiO_2 solar cell, however, we have encountered differences in performance and stability between similar cells based on flexible and glass substrates. In order to improve on this a systematic study is performed to analyze the various effects. With respect to the glass version there are a number of differences. The main aspects with respect to performance and stability are:



- PET/ITO substrate versus glass/SnO_2:F,
- sintering at temperatures below 200 °C versus at 450 °C, different TiO_2 preparation procedures are required
- electrochemical Pt versus thermal Pt.

Of major concern is the possibility of the substrate to withstand high temperatures. In the glass-based process the titaniumdioxide layer is sintered at 450 °C. As the use of a plastic substrate does not allow these high temperatures, an alternative sintering process has been developed which is conducted at temperatures below 200 °C. Though these cells still have a sufficient performance, enough to power several indoor applications, cell output currents are significantly reduced (i.e. I_{sc} is around half of the regular values), probably caused by the smaller contact area between the TiO_2 particles which constitute the nanoporous film. In a recent study the influence of the sintering temperature on the cell performance was stated to be neglectible [3].

Apart from the influence of this low sintering temperature on the cell performance, this method of sintering could also influence the stability of the solar cells. Sintering is essential to establish sufficient adhesion between the TiO_2 particles to prevent the nanoporous structure from falling apart into individual particles or peeling off of the substrate. In this investigation the stability of the solar cells based on low temperature TiO_2 is compared to the stability of the cells containing TiO_2 sintered at 450 °C. The cells have been under constant illumination of a sulphur lamp with an intensity of approximately three times direct sunlight, the cell were actively cooled to room temperature during the illumination. Up to now, the stability of the flexible substrates was restricted to several weeks, whereas for the glass version over 10000 h was reached. A remarkable outcome of the experiments with glass cells was that apparantly quite large amounts (5%) of water can be tolerated in the electrolyte as long as the proper constituents (e.g. tertiair butyl pyridine) are present [4]. The sensitivity for water has been one of the major concerns with respect to the flexible cells.

References

[1] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrey-Baker, E. Müller, P. Liska, N. Vlachopoulos and M.

[2] P.M. Sommeling , M Spath, J.A.M. van Roosmalen, T.B. Meyer, A.F. Meyer, Proceedings of the 2nd world conference and exhibition on photovoltaic solar energy conversion, Vienna, 6-10 July, 1998, 288-291
[3] F. Pichot, S. Ferrere, R.J. Pitts, B.A. Gregg, J. of the Electrochem. Society, 146 (11) 4324-4326 (1999)
[4] E. Rijnberg, J.M. Kroon, J. Wienke, A. Hinsch, J. van Roosmalen, B. Scholtens, J.G. de Vries, C.G. de Koster, A. Duchateus, I. Maes, H. Henderickx, Proceedings of the 2nd world conference and exhibition on photovoltaic solar energy conversion, Vienna, 6-10 July, 1998, 47-52

Fabrication of Quasi-Solid-State Dye-sensitized TiO_2 Solar Cells Using Ion-conductive Polymer

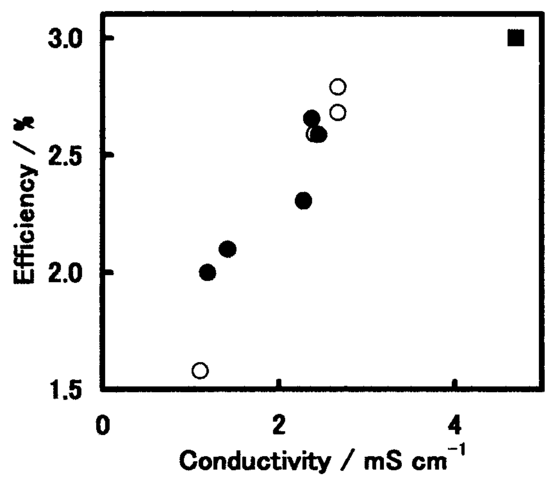
Masamitsu Matsumoto, Shingo Kambe, Wataru Kubo, Yasuteru Saito, Tkanori Kitamura, Yuji Wada, Kouichiro Shigaki†, Teruhisa Inoue†and Shozo Yanagida*

Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

† Nihon Kayaku Co., Ltd. 3-26-8 Shimo, kita-ku, Tokyo 115-0042, Japan

Dye-sensitized TiO_2 solar cells were currently under intense investigation because of their low cost and earth-friendly photovoltaics with high efficiency comparable to that of silicon solar cells. The major drawback of the module is the use of the liquid electrolytes for hole transport from dye molecules to a counter electrode. The long-term durability of the module was limited by leakage of the liquid electrolyte phase because of its difficulty in sealing of the module. Previously, we reported a quasi-solid-state dye-sensitized TiO_2 solar cell using poly(hexaethylenglycole methacrylate) as a self-crosslinking ion-conductive polymer. However, the photo-energy conversion efficiency of the cell under AM1.5, 1 kW /m^2 was relatively low compared to those using the liquid electrolyte.

Now, we report quasi-solid-state dye-sensitized TiO_2 solar cells that were fabricated with controlled crosslinking ion-conductive polymer. The procedure is as follows. Monomer solutions were prepared by mixing methoxy-origoethylenglycole methacrylate (ECA or PME), octaethyleneglycole dimethacrylate (PEG), Darocua 1173 and methoxy propionitril (MPN) as a monomer, a crosslinking reagent, a photo radical initiator and a plastisizer, respectively. The monomer solution was introduced to the cell consisting of a dye-anchored TiO_2 electrode and a platinum coated counter electrode, and was polymerized by irradiation for 5 min with solar-simulator (AM1.5, 1 kW/m^2). The resulting cell was immersed into the electrolyte solution containing iodine (0.1 M), lithium iodide (0.1 M), 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) and 4-tert-butylpyridine (1 M) for 12 hours. The relationship between photo-energy conversion efficiency and conductivity of polymer electrolyte is shown in Fig. The efficiency was increased as increasing the conductivity and was reached to 2.7 %, which is the 90% level of the cell with the liquid electrolyte.



Relationship between photoenergy conversion efficiency and conductivity of the polymer.
Closed circle : series of PME / PEG = 6 /4
Open circle : series of ECA / PEG = 9 /1
Square : liquid electrolyte

Electron Transport in Dye-sensitized Nanocrystalline TiO_2 Solar Cells

Jao van de Lagemaat,[a] Eric A. Schiff,[b] and Arthur J. Frank[a]

[a]National Renewable Energy Laboratory, Golden, Colorado 80401, and

[b]Department of Physics, Syracuse University, Syracuse, New York 13244

The rate of electron transport is a major determinant of the overall efficiency of dye-sensitized nanocrystalline TiO_2 solar cells. Following their injection into the conduction band of TiO_2 from optically excited dye molecules, electrons can either diffuse through the particle network to the charge-collecting back contact or react (recombine) with redox species (e.g., I_3^-) or dye molecules at the nanoparticle/redox electrolyte interface. Because the collection of electrons competes with recombination, slow electron transport can lead to a low charge-collection efficiency and hence a low conversion efficiency. A quantitative description of electron-transport kinetics is thus important not only for improving cell performance, but also for understanding the fundamental nature of the electron-transport process in nanocrystalline semiconductor thin film based photoelectrochemical solar cells.

This paper describes experimental and theoretical studies aimed at elucidating the mechanism of electron transport in nanoporous TiO_2 films. An analytical model is invoked that assumes that electrons undergoes multiple trapping-detrapping events, involving an exponential distribution of trap states, during their transit through the nanocrystalline film. It is shown that this model accounts quantitatively for the observed non-linear dependence of the electron transport rate on the light intensity. Further information on electron transport is obtained using Monte-Carlo type simulations. In addition to verifying the essence of the analytical model, the simulations indicate that shallow electron traps – those located close to the conduction band – strongly influence the transit time of electrons. The extent of contribution of these is found to depend on the film thickness, light intensity, energy distribution of electron traps, and temperature. The predictions of the Monte-Carlo approach were verified by time-of-flight and intensity-modulated photocurrent spectroscopy measurements.

Ambipolar diffusion of photocarriers in electrolyte-filled, nanoporous TiO_2

N. Kopidakis, E. A. Schiff,* and Q. Yuan

Department of Physics, Syracuse University, Syracuse NY 13244

N.-G. Park, J. van de Lagemaat, and A. J. Frank

National Renewable Energy Laboratory, Golden, CO 80401

Abstract

We report transient photocurrent measurements on solar cell structures based on dye-sensitized, porous TiO_2 films filled with a liquid electrolyte. The measurements are interpreted using the ambipolar diffusion concept. Ambipolar diffusion, which dates to the earliest days of semiconductor physics, describes the motion of electrons strongly coupled by electrostatic attraction to a sea of mobile, positive charges. The ambipolar diffusion coefficient in the present measurements is dominated under most conditions by electrons diffusing in the TiO_2 matrix. We report a strong dependence of the ambipolar diffusion coefficient upon the photoexcitation density, as has been proposed previously. The coefficients vary from 10^{-8} cm^2/s at low density to 10^{-4} cm^2/s for densities of 10^{18} cm^{-3}. At a specified photoexcitation density, ambipolar diffusion coefficients measured using weak laser pulses and optical bias are about ten times larger than coefficients measured using large intensity laser pulses; this latter effect challenges current models for diffusion in nanoporous TiO_2.

*Presenting author: Schiff@physics.syr.edu, tel: (315) 443-3901, fax: (315) 443-9103.

Influence of Charge Transport and Recombination on the Photocurrent Conversion Efficiency of Dye-Sensitized Nanocrystalline TiO_2 Solar Cells

J. van de Lagemaat, N.-G. Park, and A. J. Frank

National Renewable Energy Laboratory, Golden, Colorado 80401

Under bright sunlight (AM 1.5), high-efficiency dye-sensitized nanocrystalline TiO_2 solar cells with the N3 or N719 dye can supply a current density above 18 mA/cm^2 at a voltage of about 0.5 V. However, most cells deliver a current density much less than 18 mA/cm^2. A low photocurrent density indicates a low incident photon-to-current conversion efficiency (IPCE) in the spectral region, where the dye absorbs strongly. The IPCE is determined by the light absorption efficiency of the dye, the quantum yield of electron injection, and the efficiency of collecting the injected electrons at the back contact. Absorption of light by the dye in practical cells is difficult to measure. Even if the amount of light absorbed by the cell is measured accurately, it is difficult to determine the separate fractions of incident light absorbed by the dye, the electrolyte, and the TiO_2. Only light absorbed by the dye is expected to contribute to the short-circuit photocurrent. When an electron is injected into TiO_2 it can either react with the redox electrolyte or enter the external circuit via the charge-collecting back contact. The recapture of an electron by the oxidized dye is usually prevented by an even faster neutralization of the oxidized dye by the redox electrolyte. Low photocurrent is therefore the result of either inefficient light harvesting by the dye, inefficient charge injection into TiO_2, or inefficient collection of injected electrons. It is difficult experimentally to determine which of the three efficiencies (light absorption, charge injection, and charge collection) limit the IPCE. From a practical perspective, if one could eliminate one of the three factors as a cause of the low IPCE, effort could be directed toward modifying the cell conditions to improve the other two.

In this paper, we discuss a simple statistical model relating the time constants for recombination and charge collection to the charge-collection efficiency h_{cc} and the IPCE over a wide range of applied bias. Electrical impedance spectroscopy and intensity-modulated photocurrent spectroscopy are used to measure the time constants for the recombination and collection of photoinjected electrons. As the applied bias is varied from short-circuit to open-circuit conditions at one-sun illumination, recombination becomes faster, the collection of electrons becomes slower, and the IPCE decreases. The drop off of IPCE correlates with the decline of the charge-collection efficiency (h_{cc}). Over a wide range of charge-collection efficiencies (h_{cc} > 20%), the dependence of the respective time constants on h_{cc} can be described by a simple relation. At open circuit, h_{cc} is only 45 % of its short-circuit value, indicating that the dye-sensitized nanocrystalline TiO_2 solar cells do not behave as ideal photodiodes.

Morphology and Sensitization Behavior of Squaraine Dyes on van der Waals Surfaces

Norihiko Takeda Michele Stawasz and Bruce A. Parkinson

Department of Chemistry
Colorado State University
Fort Collins, CO 80523-1872, USA

We present results directed at the determination of the molecular level organization of sensitizing dye molecules on semiconductor surfaces. Dye morphologies and photosensitization properties on the SnS_2 single crystals were studied with atomic force microscopy (AFM) and photoelectrochemical measurements. Squaraine dyes were deposited on van der Waals surfaces of SnS_2 single crystals and HOPG by two methods, dipping in a dye solution and evaporation of dye solution. AFM experiments in air revealed distinct morphologies of dye aggregates and photocurrent measurements in aqueous electrolytes showed correspondingly different photocurrent spectra that could be assigned to the various surface morphologies. Spectral differences between these dye aggregates are explained by differences in intermolecular interactions. The squaraine dye layers on HOPG surfaces showed remarkable cyclic voltammetry. Monolayers of squaraine dye molecules gave very sharp oxidation and reduction peaks that were separated by over a hundred millivolts. Multiple sharp reduction peaks can often be observed up to several hundred millivolts negative of the main reduction peak. Scanning probe microscopies reveal that the dye layers consist of domains of oriented molecules. The multiple reduction peaks are attributed to the stochastic reduction of the small oriented domains due to a nucleation-limited reorganization required for expelling the anions incorporated during the oxidation process. Repeated oxidation-reduction cycles resulted in the loss of the stochastic reduction currents presumably due to annealing the surface into larger domains. Molecular resolved STM images reveal structural differences between the oxidized and reduced monolayers. The oxidation and reduction potentials are strongly dependent on the identity and concentration of the anion present in the electrolyte. The implications of these results on the spectral sensitization of semiconductors by adsorbed dye layers will be discussed.

Photosensitization of TiO_2 by Iron(II) Bipyridyl Complexes

Sue Ferrere
Center for Basic Sciences
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401 U.S.A.

Adsorbed molecular species exhibit unprecedented rates of photoinduced electron transfer into the conduction band of nanocrystalline TiO_2 in the dye sensitized solar cell. Because the electron injection rates are competitive with vibrational relaxation, it makes possible the use of photosensitizers with very short excited state lifetimes or otherwise "poor" photophysics. Iron bipyridine is one such system. Despite their extremely short excited state lifetimes, there are numerous practical and fundamental repercussions to the development of iron bipyridyl complexes as photosensitizers. While electron transfer from equilibrated excited states is well understood, there are few systems that exhibit reactivity from upper photoexcited states. From a practical standpoint, iron is substantially cheaper and much more abundant than ruthenium. We have shown that numerous iron bipyridyl complexes can sensitize nanocrystalline TiO_2 with relatively high efficiencies. We are seeking to more fully understand the structural and environmental parameters that control the ability of these systems to effect efficient photoconversion. Recent results will be discussed.

Dependence of the Quantum Efficiency of Dye Sensitized Solar Cells on the Incident Light Intensity

Thorsten Trupke and Peter Würfel
Institut für Angewandte Physik, Universität Karlsruhe
Kaiserstraße 12, 76128 Karlsruhe, Germany

The incident photon to current conversion efficiency (IPCE) of dye sensitized solar cells is measured as a function of the incident photon current density $j_{\gamma,inc}$. Dye sensitized solar cells from the INAP in Gelsenkirchen, Germany and from the FMF in Freiburg, Germany were investigated.
A typical dependence of the IPCE on $j_{\gamma,inc}$ is observed for all cells investigated in our study. A strong decrease of the IPCE from its saturation value by a factor of ten is found for low incident photon current densities $j_{\gamma,inc} < 10^{16} cm^{-2} sec^{-1}$ and for very large incident photon current densities $j_{\gamma,inc} > 10^{18} cm^{-2} sec^{-1}$.
The decrease of the IPCE at large light intensities is due to the diffusion limitation of the electrolyte inside the nanocrystalline TiO_2-electrode. This explanation is confirmed by time resolved measurements of the photocurrent after an illumination is switched on. The photocurrent transients are characteristic for diffusion limited current. As the decrease of the quantum efficiency occurs at absorbed light intensities, which are substantially larger than under typical solar illumination conditions this decrease of the IPCE is not critical for the functioning of the cell.
Contrary the decrease of the IPCE at low incident light intensities has consequences for the efficiency of dye sensitized solar cells for low illumination levels e.g. for indoor applications. This decrease is assigned to the recombination of photoinjected TiO_2-conduction band electrons with the oxidizing ions in the eletrolyte via surface states. At large incident light intensities the filling of trap states results in a saturation of the IPCE. This interpretation is confirmed by a numerical model.
We find that measurements of the IPCE using an experimental technique where the cell is illuminated with intense constant bias light and the IPCE is measured with low intensity, modulated, monochromatic light yield the saturation value of the IPCE at each wavelength.
Our investigation shows that great care has to be taken, when the IPCE of dye sensitized solar cells and of nanocrystalline electrodes in general is measured. If the measurements are carried out with DC illumination only, one must be aware of the dependence of the results on the incident light intensity. Too low monochromatic light intensities result in an underestimation of the IPCE. If the results shall be used e.g. to calculate the short circuit current of a cell under illumination the method with bias light and low intensity modulated monochromatic light yields more realistic results.
Our measurements are at variance with measurements by A.C.Fisher et al. which have been published recently[1] where the IPCE of dye sensitized solar cells has been measured to be only weakly dependent on the incident photon current density over five orders of magnitude of incident light intensity. The origin of this apparent discrepancy remains to be cleared.

(1) A.C.Fisher, L.M.Peter, E.A.Ponomarev, A.B.Walker, K.G.U.Wijayantha., *J.Phys.Chem B*, **2000**, 104, 949

The Characteristics of Electron Transport and Light Scattering of Nanocrystalline TiO_2 Electrode with a New Porous Structure

Yuan LIN, DongShe ZHANG, JingBo ZHANG, XuRui XIAO, BaoWen ZHANG, Yi CAO
(Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101,China)

Nanocrystalline semiconductor thin film as a new kind of particulate semiconductor electrode have attracted considerable research interest. This film consists of interconnected nanocrystalline semiconductor particles to construct a highly porous network structure. Recent studies revealed that the porous network structure plays an important role in determining the photoelectrical properties of nanocrystalline electrodes due to its strong effects on the electron transport and light scattering. In this work, we studied the characteristics of electron transport and light scattering of nanocrystalline TiO_2 electrode with a new porous structure.

A new porous structure of nanocrystalline TiO_2 electrode was formed by coating a mixture of TiO_2 nanoparticles with small size ~10nm and large size ~100nm in a suitable proportion on conducting glass substrates and followed with sintering as usual. The photoelectrical properties were studied in dye-sensitized solar cells. Nanoparticles with small size are responsible for a large surface area, which can be sufficient for adsorption of a monolayer of dye, and the large size nanoparticles are used to increase the light scattering. Nanocrystalline electrodes consisting of the mixtures of binary TiO_2 nanoparticles 10nm and 100nm in the ratio of 95:5 and 85:15 (10nm:100nm, by weight) were fabricated resulting in a thinner film thickness of 5μm. An increase of light absorption at 400-750nm wavelength in the absorption spectra of both electrodes compared to the electrode consisting only of 10nm nanoparticles with thickness of 8μm is offered by the light scattering. These results indicate that the light scattering of TiO_2 nanoparticles can increase the light adsorption efficiently in a thinner dye sensitized nanocrystalline TiO_2 film.

Electron transport was studied by IMPS. The results show that the electron transport rates of both electrodes consisting of binary TiO_2 nanoparticles were faster obviously than that of the 10nm nanoparticulate TiO_2 electrode, due to the decreases in both of transport distance and probability of trapping in the thinner film. Electron transport rates of binary particulate electrodes were further increased via $TiCl_4$ post-treatment. More than 2 times increase of electron transfer rates after $TiCl_4$ post treatment indicates that the density of trapping center in the nanocrystalline TiO_2 particles were effectively diminished during the chemical treatment process.

The effective light scattering and the improvement of electron transport in the new porous structure of nanocrystalline TiO_2 electrode lead to an increase of the incident photo to current efficiency (IPCE) appreciably.

Acknowledgment: This work was supported by the Dean grant of Chinese Academy of Sciences and Photochemistry Lab of Chinese Academy of Sciences.

Electrochromic Devices Based on Wide Band-Gap Nanocrystalline Semiconductors Functionalized with Polynuclear Mixed Valence Compounds

C. A. Bignozzi*, R. Argazzi, M. Biancardo, M. Costa, V. Ferri

Department of Chemistry University of Ferrara, 44100 Ferrara Italy

The general concept of using polynuclear mixed-valence compounds anchored to nanocrystalline wide band-gap semiconductors for their use as electrochromic devices is introduced. This idea is applied to control the domain of the electro-induced spectral changes in the whole visible and near infrared regions.

Numerous binuclear, and more in general polynuclear, mixed-valence compounds based on transition metal ions have been reported since the synthesis of the Creutz ion $[Ru^{II}(NH_3)_5pzRu^{III}(NH_3)_5]^{5+}$. (**1**) The peculiar property of this polynuclear species, relevant for their application in electrochromic devices, is related to the presence of metal-to-metal absorption bands in the visible and near-infrared spectral regions. These bands, which are also known as intervalence transfer bands, are due to optical electron transfer transitions involving bridged metal centers.

Adsorption of polynuclear mixed-valence compounds on transparent nanocrystalline SnO_2 or TiO_2 films, deposited on conductive glass, results in electrochromic devices where the electronic transitions localized on the metal sub-units and the electronic transitions between the metal centers can be controlled by the applied potential. Modulation of the transmitted light over the whole visible and NIR spectral regions can be obtained by synthetic design of the polynuclear species.

Reference

Carol Creutz, Progr. Inorg. Chem. **1983**, *30*, 1

Dynamics of Semiconductor-to-Dye Electron Transfer for Carboxy-Anthracene Dyes Bound to Different Sized TiO_2 Particles

Gregory V. Hartland, Ignacio Martini,* and José H. Hodak

Department of Chemistry and Biochemistry, University of Notre Dame, 251 Nieuwland Science Hall, Notre Dame, IN 46556-5670

Abstract: The electron transfer dynamics for the 1-, 2- and 9-isomers of anthracenecarboxylic acid bound to different sized anatase-TiO_2 particles has been examined by ultrafast transient absorption spectroscopy. The results from these measurements show that: (i) greater than 85% of the back (semiconductor-to-dye) electron transfer reaction is complete within 100 ps, and that in this time range the observed decays in the transient absorption data can be fitted using a single exponential decay plus an offset. (The offset accounts for the unbound dye molecules.) (ii) The size of the TiO_2 particles does not affect the electron transfer dynamics for particles in the 4 nm to 40 nm size region. A simple model where the electrons are assumed to be evenly distributed over the surface of the particle could not reproduce the experimental results. Thus, these experiments show that the electrons are trapped in localized states, that must be adjacent to the binding site for the dye radical cation, i.e., their spatial distribution is not random. The trapped electrons undergo back electron transfer before they can diffuse away from the dye radical cation. These results also show that the shape of the nanoparticles should have very little effect on the semiconductor-to-dye electron transfer times for this system. The observation of essentially single exponential decays for the back electron transfer reaction in our data also implies that the trap sites for the electrons at the surface of the particle have a fairly narrow distribution in energy.

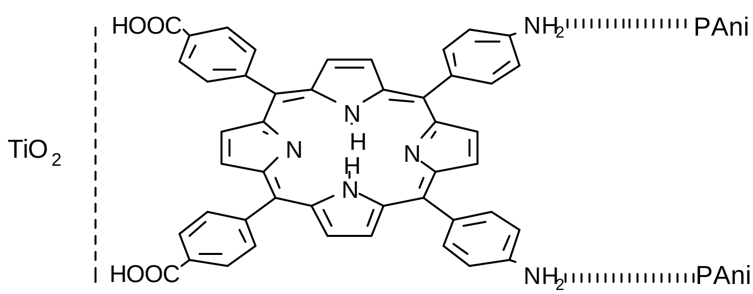
*Current address: Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90095-1569

Photoelectropolymerization of Aniline with Porphyrin-sensitized TiO_2 Electrodes

Carl C. Wamser,* Grant Yang, and Hooi-Sung Kim

Department of Chemistry, Portland State University, Portland, OR 97207

In an effort to create a solid-state version of the Grätzel cell, we have been investigating the prospects of generating a conductive polymer in the pore spaces of the nanoparticulate electrode. Porphyrin photosensitizers have been prepared with various combinations of carboxy and amino substituents, where the carboxy groups adsorb to TiO_2 and the amino substituents are used to anchor an electron donor system. The cis-dicarboxydiamino derivative (TC_2A_2PP), shown below, illustrates the dual functionality desired.



Preliminary experiments have been performed with the tricarboxymonoamino derivative (TC_3APP), which was the first of the mixed sensitizers isolated in pure form. Adsorption of the sensitizer onto a nanoparticulate TiO_2 electrode, immersion in an aniline solution containing electrolyte, acid, and poly(ethylene oxide), and irradiation with visible light leads to a photocurrent that grows and then levels off. The finished cell operates with an open-circuit photopotential of about 0.5 V and a short-circuit photocurrent of about 100 $\mu amp/cm^2$ (at an irradiance of about 0.3 sun). Experiments are underway to elucidate the processes that are occurring in the cell as well as to optimize its efficiency as a solar cell.

Organic Dye-sensitized Oxide Nanocrystalline Semiconductor Solar Cells: Their Photovoltaic Performance and Charge Recombination Kinetics

Kohjiro Hara[a], Ryuzi Katoh[a], Takaro Horiguchi[b], Tohru Kinoshita[b], Kazuhiro Sayama[a], and Hironori Arakawa[a]

[a]*National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

[b]*Sumitomo Osaka Cement Co. Ltd., 585 Toyotomi, Hunabashi, Chiba 274-8601, Japan*

Graetzel and co-workers reported that a dye-sensitized solar cell based on cis-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (N3 dye) as a photosensitizer and nanoporous TiO_2 thin film electrodes with an iodine redox electrolyte showed a highly efficient solar energy conversion to electricity of 10% under 1 sun (AM 1.5) [1]. Recently dye-sensitized solar cell using organic dyes as the photosensitizer have been positively investigated because of low cost compared to Ru complexes. We have examined organic dyes such as eosin yellow (EY) and mercurochrome (MC) as the photosensitizer for dye-sensitized nanocrystalline oxide semiconductor solar cells.

EY and MC-sensitized nanocrystalline oxide semiconductor solar cells with an iodine redox electrolyte showed good photovoltaic performance [2-4]. For instance, a 2.5% solar energy conversion efficiency was accomplished for a MC/ZnO solar cell under AM 1.5 (99 mW cm^{-2}) with a short-circuit photocurrent density of 7.44 mA cm^{-2}, an open-circuit photovoltage of 0.52 V, and a fill factor of 0.64. The solar cells can convert efficiently visible light in the range from 400 to 600 nm to current. The maximum IPCE (incident photon-to-current conversion efficiency) reached 69%, which is equal to that for the N3 dye/TiO_2 solar cell, at 510 nm for a MC/ZnO solar cell. The transient absorption of MC adsorbed on TiO_2 and ZnO substrates indicated that the back electron transfer from the conduction band of semiconductors into oxidized MC (i.e. charge recombination) occur very slowly. So high IPCE for the MC/ZnO solar cell would be due to a successful charge separation with a fast electron injection from excited state of MC to the conduction band of ZnO and a slow back electron transfer process as well as the N3/TiO_2 system.

References

[1] Md. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, and M. Graetzel, *J. Am. Chem. Soc.*, **115**, 6382 (1993).

[2] K. Sayama, M. Sugino, H. Sugihara, Y. Abe, and H. Arakawa, *Chem. Lett.*, 753 (1998).

[3] K. Hara, T. Horiguci, T. Kinoshita, K. Sayama, H. Sugihara, and H. Arakawa, *Chem. Lett.*, in press.

[4] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, and H. Arakawa, *Solar Energy Materials and Solar Cells,* submitted.

Newly Prepared Tris-Chelating β-Diketonato Ruthenium Complexes as Highly Efficient Photosensitizers for Nanocrystalline TiO_2 Solar Cells

Yoshiaki Takahashi, Hironori Arakawa, Hideki Sugihara, Kohjiro Hara
National Institute of Materials and Chemical Researches. 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

There is currently considerable interest in ruthenium complex-sensitized nanocrystalline TiO_2 solar cell because of their remarkably high light-to-electrical energy conversion efficiency.[1] Among numbers of polypyridyl-ruthenium based coordination compounds, the best performing sensitizer employed for such an application have been a *cis*-dithiocyanatobis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium complex.[2] Recently we have started investigating the effect of the mono- and bidentate ligand as well as metal in that complex on photoelectric conversion with the aim of understanding the photoelectrochemical process and improving the solar cell efficiency.[3] Here, we report the syntheses and properties of several β-diketonate complexes, (β-diketonato)bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium. We can expect following advantages by attaching the β-diketonate ligand instead of thiocyanates to central metal coordination sphere:

(1) Enhanced spectral response over broad range of solar spectrum owing to strong σ-donating character of the negatively charged β-diketonate ligand.
(2) Long-term stability of the complexes derived from tris-chelating structure.
(3) Readily tunable ruthenium ground state energy level by an appropriate choice of the substituents at the β-diketonate ligand.

As a result, they exhibit very efficient energy conversion.

β-Diketonate complexes were obtained in good yield by heating the mixture of *cis*-dichlorobis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium and corresponding β-diketone in the presence of base. The electronic spectra of them display two MLCT absorption maxima in the visible region with molar extinction coefficients beyond 10^4 $M^{-1}cm^{-1}$. Notably, the positions of the lower energy MLCT band maxima were red-shifted compared to dithiocyanate complex in spite of positive charge on ruthenium. Electrochemical measurements showed reversible one electron process at around 0.7 V versus SCE correspond to Ru(III/II) couple suggesting redox stability of these complexes. Nanoporous TiO_2 thin films modified by β-diketonate complexes generate large photocurrent and photovoltage under irradiation of AM 1.5 sunlight. Thus light-to-electric energy conversion efficiency of 6.0 % was attained with acetylacetonate complex while almost the same value were observed for dithiocyante complex under our measurement condition.

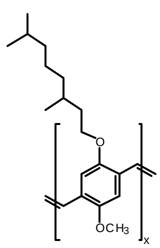
References

(1) Kalyanasundaram, K.; Grätzel, M. *Coord. Chem. Rev.* **1998**, *77*, 347.
(2) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
(3) (a) Sugihara, H.; Singh, L. P.; Sayama, K.; Arakawa, H.; Nazeeruddin, Md. K.; Grätzel, M. *Chem. Lett.* **1998**, 1005. (b) Islam, A.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Murata, Y.; Takahashi, Y.; Sugihara, H.; Arakawa, H. *Chem. Lett.* in press. (c) Islam, A.; Arakawa, H. *New J. Chem.* submitted for publication.

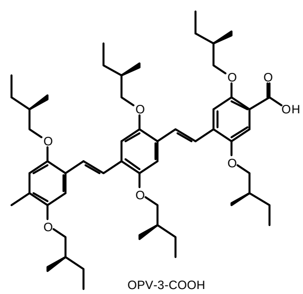
PHOTOINDUCED ELECTRON TRANSFER FROM PPV POLYMERS AND OLIGOMERS TO TiO_2

M. M. Wienk[1]; B.M.W. Langeveld[2]; P.A. van Hal[3]; R. A. J. Janssen[3]; J. M. Kroon[1]
[1]ECN Solar Energy, P.O. Box 1, 1755 ZG, Petten, The Netherlands, wienk@ecn.nl
[2]TNO Industries, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands
[3]Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

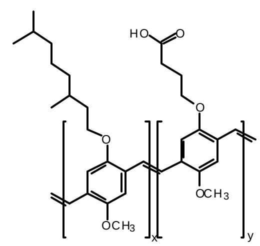
One of the main factors determining the efficiency of dye sensitized solar cells is the use of nanoporous films with a large internal surface between the electron accepting semiconductor (e.g. TiO_2) and the electron donating dye. In addition, the so-called "bulk D-A heterojunction" photovoltaic cells benefit from an extended interface between electron donor and acceptor. Herein, the phase-separated network morphology of a π-conjugated polymer and a suitable electron acceptor ensures close proximity between photoexcitation and the interface at which charge separation takes place.



MDMO-PPV



OPV-3-COOH



PPV(COOH) x

Our research focuses at the combination of nanoporous TiO_2 films with π-conjugated polymers, to make solid state photovoltaic cells. Initial work focussed on soluble polymers, like MDMO-PPV. This material is introduced into the pores of the nc-TiO_2, by solution staining. Photoinduced absorption spectroscopy (PIA) and electron spin resonance (ESR) demonstrate efficient electron injection from the polymer excited state into the TiO_2. However, due to the high molecular weight of the polymer only a minor (low molecular weight) fraction of the polymer is able to penetrate the pores, which have diameter of 10-20 nm. To circumvent this problem, oligomers like OPV-3-COOH are used. This PPV trimer has -apart from much smaller molecular dimensions- an additional carboxylic acid group to ensure high affinity for the TiO_2 surface ($K_{abs} \approx 2\ 10^5\ M^{-1}$). As a consequence, dense monolayer coverage of the TiO_2 is obtained, as well as complete fluorescence quenching, indicating very efficient electron transfer from the OPV excited state. This is confirmed by the measured IPCE values of a dye cell stained with OPV-3-COOH. Finally, carboxylic acid functionalized PPV polymers have been synthesized. Due to the acid groups and a moderate molecular weight, good penetration of the porous TiO_2 films is expected. Adsorption behavior and photophysical properties will be discussed. This work is financially supported by the Netherlands Agency for Energy en Environment (NOVEM)

Contactless photo-conductivity measurements on heterojunctions of TiO_2 and organic molecular antenna layers

Tom J. Savenije, Jessica E. Kroeze, Marion E. van Brederode,
Martien J.W. Vermeulen and John M. Warman
Radiation Chemistry Department, IRI, Delft University of Technology,
Mekelweg 15, 2629 JB, Delft, The Netherlands

For the realisation of integral solid state photovoltaic cells based on organic materials, there is a considerable interest in the use of bilayers of a wide band-gap inorganic semiconductor and a p-type organic material. On excitation of such a bilayer with visible light an exciton is created in the organic antenna layer which can dissociate at the interface, resulting in an electron in the semiconductor and a hole in the polymer. Using such a bilayer in a sandwich cell configuration, the polymer should thus function as both an antenna and as a conducting layer for hole transport to an electrode. Many processes and parameters contribute to the overall efficiency of such a device, including the exciton lifetime and diffusion coefficient, the rates of interfacial charge separation and recombination, the mobilties of charge carriers, and the wavelength dependence of photocarrier generation.

For studying these factors the application of metal electrodes often introduces additional complications, such as non-Ohmic contacts or space charge limited currents which mask the photophysical processes of interest within the bilayer itself. Recently we have developed a technique by which the charge separation within semiconductor /antenna bilayers can be monitored without the necessity of electrodes thus considerable simplifying sample preparation and data interpretation. The method depends on the use of microwaves to monitor the change in conductivity on illumination. For charge carrier generation within the bilayer monochromatic illumination is applied using either a continuous light source or a continuously-wavelength-variable, nanosecond-pulsed laser ranging from the UV to the NIR. In this way both steady-state and dynamic photoconductivity action spectra can be obtained.

Using this technique the efficiency of the light induced charge separation between a spin-coated thin dialkoxy phenylene vinylene polymer layer and a smooth thin anatase TiO_2 layer has been obtained. By comparing the conductivity transients observed at irradiation in the visible with that from direct band-gap excitation of the TiO_2 using UV light, maximum values for the IPCE of 6% are found. Furthermore, the exciton diffusion length in these conjugated polymer has been estimated to be on the order of 20 nm by studying similar samples with different thicknesses, and using front- and backside illumination. Other results dealing with the wavelength dependence of the charge carrier generation efficiency and different antenna molecules, such as porphyrins will be presented and discussed.

Photosensitization of nanocrystalline SnO_2 films by Pinacyanol H-aggregates

Said Barazzouk[1], Hong Lee[2], Prashant V. Kamat[3] and Surat Hotchandani[1]

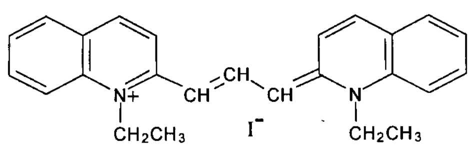
[1] Groupe de Recherche en Énergie et Informations Biomoléculaire, Université du Québec à Trois-Rivières, C.P.500, Trois-Rivières, PQ, Canada, G9A 5H7.

[2] Department of Chemistry, Won Kwang University, Iksan, Korea.

[3] Radiation Laboratory, University of Notre Dame, Notre Dame, IN., 46556, USA.

The cyanine dyes are a remarkable class of strong absorbers in the visible, and are thus highly suitable as photosensitizers in dye sensitized photoelectrochemical (DSPE) solar cells. Further, a particular characterstics of these dyes is that they easily form aggregates. In this study, we present the photoelectrochemical characterics of a DSPE cell obtained from a cyanine dye Pinaacyanol (1,1'-diethyl-2,2'-carbocyanine iodide, PCYN), shown in Scheme 1, deposited on nanocrystalline SnO_2 electrodes. Both monomer and aggregates (H-type) of PCYN are able to photosensitize SnO_2 nanocrystallites, and exhibit an IPCE (incident photon-to-photocurrent efficiency) of ~ 5%. The process of fast reverse electron transfer between the photoinjected electron in the conduction band of SnO_2 and the cation radical of the dye is believed to be the major factor for the poor IPCE of the cell.

To better understand the phenomenon of aggregation, charge injection and charge recombination, transient absorption measurements of PCYN adsorbed on SiO_2 and SnO_2 nanocrystallites were carried out. When excited with 532 nm laser pulse, a short-lived ($\tau < 30$ ps) excited state of H-aggregates of PCYN is observed on SiO_2 surface. However, a long-lived cation radical of PCYN is seen on SnO_2 surface. This cation radical formation is the result of electron injection from PCYN into SnO_2 nanocrystallites. Both singlet and triplet excited states of the dye aggregates are found to participate in charge injection process. The dependence of cation radical yield on the concentration of SnO_2 colloids and the intensity of laser excitation, and kinetics of charge injection process will be discussed.



Scheme 1. Structure of PCYN

Novel black MLCT sensitizers

Yuanjun Hou, Puhui Xie, Kuiwang Wu, Jianhua Wang, Baowen Zhang *, Yi Cao *

Institute of Photographic Chemistry, the Chinese Academy of Sciences

Beijing, 100101, People's Republic of China

The development of ruthenium(II) polypyridyl complexes sensitized solar cell exhibiting a light-to-electrical conversion efficiency of 10% has brought of the sensitization of large band gap semiconductor oxides to the forefront of photoelectrochemical research.[1-2] However, relatively weak absorption of commonly utilized in the 700 to 800 nm range inhibit a further improvement of the solar cell efficiency. One of the important goal for the next generation of solar cells base on this technology is to prepare sensitizers that could harvest light through the visible region and into the near IR.

For ruthenium diimine sensitizers, there are two design strategies to systematically shift the metal-to-ligand charge transfer (MLCT)($d\pi \rightarrow \pi^*$) absorption bands toward the red region of the solar spectrum. One is to lower the energy of π^* by adding electron-withdrawing groups to a polypyridyl ligand, and the other is to increase that of $d\pi$ by weakening of the ligand field.[3-4]

Here, the latter approach was employed and two novel black sensitizers, [Ru (4'-*p*-carboxylic acid-phenyl-2,2':6',2"-terpyridine) $(NCS)_3]^-$, and *trans*-Ru(4,4'-dicarboxylic acid-2,2'- bipyridine)$_2$(NCS)$_2$ were synthesized. The MLCT absorption bands of the above two complexes were observed at 553 nm, and 592nm respectively. The former compound efficiently sensitized TiO_2 beyond 700 nm.

Reference

[1] O'Regan, B.; Gratzel, M. *Nature* **1991**, 353, 737

[2]Nazeeruddin,M.K.;Kay,A.;Rodicio,I.;HumphryBaker,R.;Muller,E.;Liska,P.; Vlachopoulos, N. and Gratzel,M. *J.Am.Chem.Soc.* **1993**,115,6382

[3] R. Argazzi; C. A. Bignozzi; T. A. Heimer; F. A. Castellan; G. J. Meyer *Inorg.Chem.* **1994**, 33 ,5774

[4]Hou, Y.J.; Xie, P.H.; Zhang, B. W.; Cao, Y.; Xiao, X.R.; and Wang, W.B. *Inorg.Chem.* **1999**, 38, 6320

Enhanced Stability of Photocurrent-Voltage Curves in Ru(II)-Dye-Sensitized Nanocrystalline TiO_2 Electrodes with Carboxylic Acids

Tae-Sik Kang, Kyung-Hee Chun, Jin-Sup Hong, Sun-Hee Moon, and Kang-Jin Kim
Department of Chemistry, Korea University, Seoul 136-701, Korea

Although stability is one of the basic requirements for practical application of dye-sensitization TiO_2 cells to solar energy conversion, stability studies have not drawn much attention. The ruthenium-dye based sensitization solar cell, in fact, was found to be photoelectrochemically instable according to a recent report by Grünwald and Tributsch.[1] They found that ruthenium complexes attached to TiO_2 are photoelectrochemically transformed and irreversibly consumed under condition of insufficient regeneration of the oxidized dye molecules by the reaction with iodide ions.

In this paper, we report instable photocurrent-voltage curves of a $[RuL_2(NCS)_2]$ dye-coated TiO_2 electrode in I/I_3^- acetonitrile solution with illumination for a relatively short period of time, and apparent stabilization obtained by adding carboxylic acid into the solution.. The stabilization is primarily discussed in terms of adsorption of carboxylic acid on the TiO_2 surface based on the measurements by photocurrent-voltage characteristics, UV-Vis absorption and reflectance, flat band potential, and ac impedance.

Addition of carboxylic acid in the solution leads to a dramatic improvement in the stability together with increase in the short-circuit photocurrent (J_{sc}) and decrease in the open-circuit photovoltage (V_{oc}) as shown in Fig. 1. Mechanism of the stability enhancement and variation in the J-V curves have been studied by using absorption and ac impedance spectroscopies. The measurements reveal that adsorption of carboxylic acid on the TiO_2 surface plays an important role in improving the stability as well as changing the J-V curves. The adsorbed triiodide ions on the TiO_2 surface in the absence of carboxylic acid are apparently replaced with carboxylic acid at high concentration. The enhanced stability can be attributed to the reduction of back electron transfer to I_3^- and the inhibition of further adsorption of I_3^- ions as a result of adsorption of carboxylic acid. The replacement of triiodide ions with carboxylic acid results in lowering the flat band potential (V_{fb}) of the electrode followed by decreasing the V_{oc}. The lowering V_{fb} leads to a positive shift of the conduction band edge of TiO_2, which permits an increased driving force for electron injection from the excited dye, explaining an increase in the J_{sc} upon addition of carboxylic acid.

1. R. Grünwald and H. Tributsch, *J. Phys. Chem. B*, **101**,2564(1997).

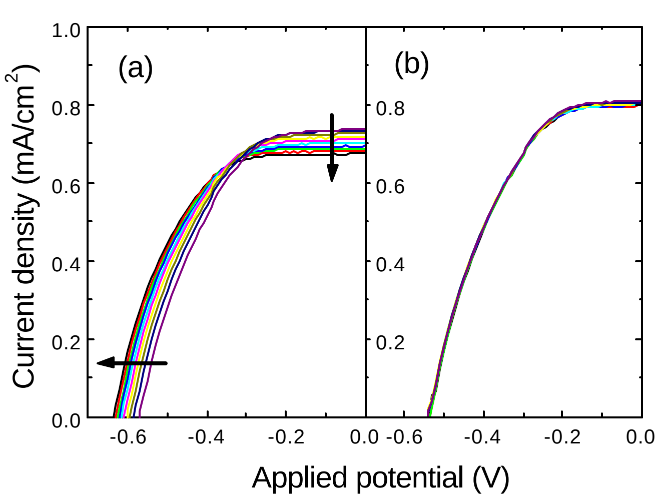


Fig. 1. Dependence of photocurrent-voltage curves of a $[RuL_2(NCS)_2]$ dye-sensitized TiO_2 cell in 0.06 M LiI/3 mM I_2 acetonitrile on the recording number. Scan rate was 100 mV/sec: (a) in the absence and (b) in the presence of 0.17 M acetic acid. Arrows indicate the direction of increasing the recording number.

DYE-SENSITIZED NANOCRYSTALLINE Ti-OXIDE-BASED SOLAR CELLS PREPARED BY SPUTTERING: INFLUENCE OF THE SUBSTRATE TEMPERATURE DURING DEPOSITION

M.M. Gómez[a], J. Lu[a], J.L. Solis[a], E. Olsson[a], A. Hagfeldt[b], and C.G. Granqvist[a]

[a]Department of Materials Science, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden

[b]Department of Physical Chemistry, Uppsala University, P.O. Box 532, SE-751 21 Uppsala, Sweden

Abstract

Nanocrystalline Ti oxide films were prepared by DC magnetron sputtering from a metallic Ti target plate positioned 13 cm from a substrate holder. The films were deposited onto glass substrates precoated with a layer of transparent and conducting SnO_2:F. During the deposition, the substrate temperature t_s was set at a constant value in the $50 < t_s < 300^oC$ range. The characterization of the films was carried out using X-ray diffraction, infrared absorption spectroscopy, atomic force microscopy, and transmission electron microscopy. The solar cells conversion efficiency h was measured after dye sensitization of the films in cis-dithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II). The dye incorporation was dependent upon t_s, and an optimum of h = 1.7 % was found with ~0.8 μm thick Ti oxide films prepared at 250^{o}C; the microstructure then displayed a well defined parallel penniform pattern. The crystallite size was substantially enlarged at $t_s > 250^oC$, and h showed an ensuing decrease. Infrared absorption spectroscopy demonstrated that the density of OH groups did not strongly influence the interaction between Ti oxide and the dye.

Poster presentation

Electrochemical impedance of nanoporous TiO_2 dye sensitized solar cells

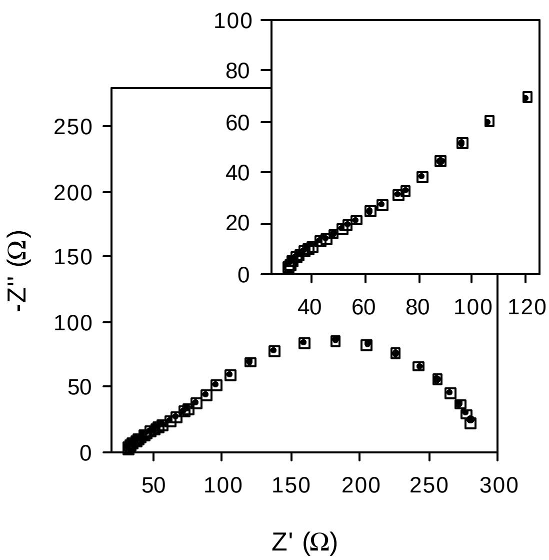
F. Fabregat Santiago[1], G. Garcia Belmonte,[1] J. Bisquert[1,]* and A. Zaban[2]

[1]Departament de Ciencies Experimentals, Universitat Jaume I, 12080 Castelló, Spain
[2]Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel.

We report here on preliminary results of electrochemical impedance measurements on nanoporous TiO_2 dye-sensitized solar cells. This research aims to clarify the electrical potential distribution, the location of the photo-electromotive force, and the influence of recombination in cell operation. We are able to provide a detailed description of measurements made in the dark at negative applied bias, where the TiO_2 has been supplied with a large quantity of electrons and recombination is enhanced. These spectra are highly structured and untrivial, as shown in the figure.

The interpretation of these spectra requires the combined used of two previously reported models for distributed equivalent circuits[1,2] which allow for good quality fits to be obtained. In the low frequency region, one finds an arc turning to a Warburg-like feature. This can be understood in terms of a porous electrode model[1] as the coupling between recombination at the surface of the particles and transport in them. At high frequency a bending of the Warburg part indicates anomalous transport of electrons.[2]

The main result is that the entire response can be attributed to transport, polarization and reaction processes occuring inside the mixed TiO_2/electrolyte phase, while the macroscopic boundaries appear to play no significant role. It is hoped that an extension of this research will help clarify the interpretation of photo-emf and will also provide a useful characterization technique.



Impedance of a nanoporous TiO_2 dye-sensityzed solar cell at –0.7 V bias in the dark. Dots are measured, squares is a fit with the model indicated in the text.

(1) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C. *J. Phys. Chem. B* **2000**, *104*, 2287.
(2) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Compte, A. *Electrochem. Commun.* **1999**, *1*, 429.

* e-mail: bisquert@uji.es

Transient Absorption Spectroscopy as a Tool to Study Electron Transport in Nanostructured TiO_2

Hans van 't Spijker, Albert Goossens and Joop Schoonman
Laboratory for Inorganic Chemistry, Faculty of Applied Sciences,
Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Dye sensitized solar cells are constructed from a network of sintered semiconductor nanoparticles on which dye molecules are adsorbed. Upon light exposure, the dye molecules harvest the light and an electrical current is generated in the nanostructured network. In these networks the mechanism of charge transport is not well understood. Transient absorption spectroscopy is a useful technique to study electron migration.

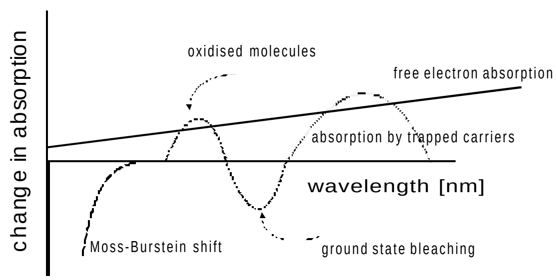


Figure 1: The contributions in transient absorption spectroscopy

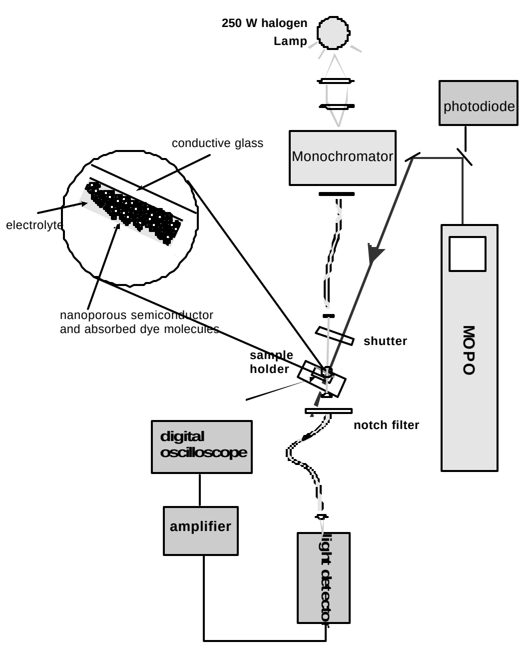


Figure 2: Schematic of the set-up for Transient Absorption Spectroscopy.

Free electrons in solids interact with photons, resulting in a pronounced absorption in the infrared. By recording the temporal change in absorption after electron injection, information on the transport kinetics can be derived. Transient absorption spectroscopy can also be used to study other phenomena. Schematically these are shown in Figure 1.

We have built a unique set-up with which absorption changes as small as 10^{-5} in the wavelength range between 300 and 5500 nm can be measured. Transients up to 100 ms can be recorded with a time resolution of ~50 ns. Figure 2 displays the measurement set-up.

The change in absorption has been recorded at several wavelengths. Figure 3 shows the wavelength dependency of the maximum absorption change. Trapped electrons (below 1200 nm) can be discerned from free electrons (above 1400 nm). Therefore, it is possible to study the kinetics of trapped electrons independent from the kinetics of free electrons.

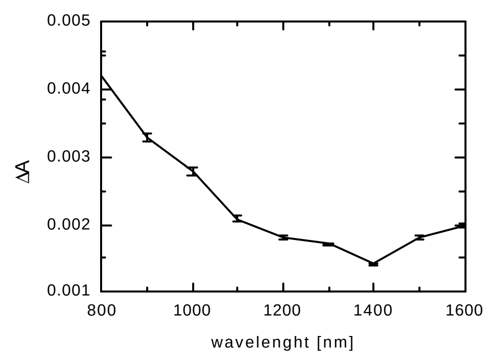


Figure 3: Wavelength dependence of absorption change in TiO_2 films immersed in 0.1 M KI acetonitril.

At this stage, the transport kinetics of free and trapped electrons in TiO_2 films have been studied at different KI and $LiClO_4$ concentrations. From these measurements a clear difference in kinetics for the trapped and free electrons is observed. Spectra recorded at different KI concentrations indicate that the free electrons are screened by the ions in the electrolyte. A more systematic study is in progress in order to elucidate the dynamics of trapped and free electrons as a function of the screening by the interpenetrating liquid phase.

Constraints on Selection of Sensitizing Dyes for Dye-Sensitized Solar Cells

M. T. Spitler, L. Stuhl, and A. Ehret

ChemMotif, Inc.
60 Thoreau St., #211
Concord, MA 01742-2411

There are many constraints placed upon a spectral sensitizer in systems of dye-sensitized solids. They depend upon the role that the dye plays in the overall energy transduction scheme of the system.

Many of these constraints are straightforward to define. For an excited sensitizing dye to effect an efficient charge separation, the redox potentials of the excited dye must be poised correctly with respect to the participating electron acceptor and donor species. Modern electron transfer theory describes the requisite thermodynamic relationships between donor and acceptor required for a fast and effective transfer of charge away from the excited sensitizer. On the other hand, if a sensitizer serves in the role of a light harvester in the system where it absorbs light and transfers the energy to a reactive dye where charge separation occurs, other constraints are evident. It must absorb in spectral regions of interest and have a physical location that allows an efficacious shuttle of this excitation to the reactive dye molecules of interest.

Other restrictions placed upon sensitizers are less obvious, but reveal themselves with some consideration of the operating mechanism of the system as a whole. For example, when an excited dye injects an electron into the conduction band of a solid, effective charge separation is only achieved when a back reaction is precluded. This may be achieved through an energetic relationship between the conduction band energy of the solid and the oxidized dye that slows down the rate of recombination. It may also be hindered by spacing the chromophore distant from the surface through intervening functional groups. A fast and effective reduction of the oxidized dye by a regenerating agent will also serve this role; this requires the proper energetic relationship between oxidized dye and regenerating agent.

However, other requirements placed on a sensitizer are more subtle and only come into evidence through experience. These can include the net charge on the dye or the mode of decomposition of the oxidized dye. The method of attachment of the dye to the surface and the chromophore's orientation can influence the spectral characteristics of the chromophore in undesired ways.

An excellent tutorial on such constraints in dye sensitized systems can be found in the restrictions placed on dyes used for the spectral sensitization of silver halide grains in photographic films. In silver halide photography, adsorbed cyanine dyes absorb light and sensitize latent image formation through injection of electrons into the solid's conduction band.

If one steps away from the primary charge separation event and adopts the perspective of the bottom line production of optical density in developed photographic film, many additional requirements are placed upon sensitizing dyes: For silver halide substrates, a sensitizer must:

- be able to inject an electron into the silver halide conduction band
- not be reduced by an electron from the conduction band
- adsorb on the silver halide grain to absorb in the desired spectral region
- have a sharp spectral cut-off in red absorption
- have an oxidation potential positive of that of the gelatin
- be a bromine acceptor
- not impede photographic development
- not color the negative

The net result of these restrictions is that only a few dozen cyanine dyes out of the tens of thousands known are suitable for use as sensitizers in photographic films.

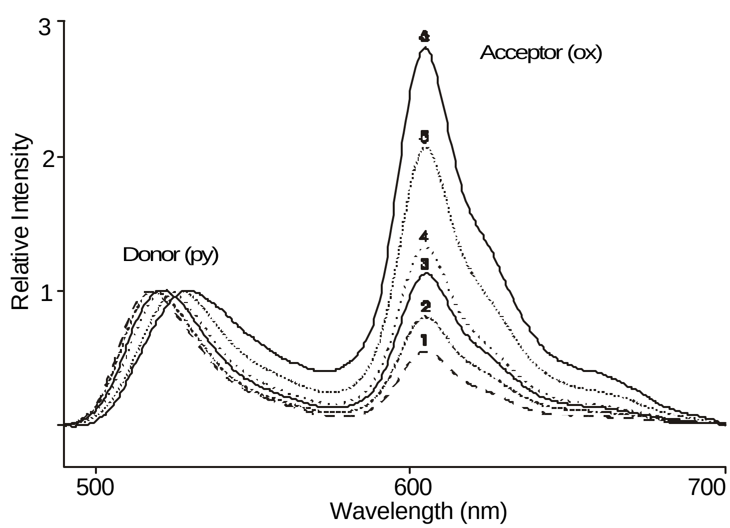
The same small ratio should be expected for dye sensitized nanocrystalline solar cells. In principle, a similar list of requirements can be compiled for sensitizing dyes in this application. This will be attempted and illustrated through experimental work that employs novel carboxylated cyanine dye in the spectral sensitization of nanocrystalline TiO_2 solar cells.

Energy Collection, Transport, and Trapping by Supramolecular Organization of Dyes

Gion Calzaferri, Silke Megelski, Marc Pauchard, Huub Maas, André Devaux

University of Bern, Department of Chemistry and Biochemistry, Freiestrasse 3, CH-3000 Switzerland

Plants are masters in the direct transformation of sunlight into energy. In the ingenious antenna system of the leaf, sunlight is transported by chlorophyll molecules for the purpose of energy transformation. We have succeeded in reproducing a similar light transport in an artificial system on a nano scale. In this artificial system, zeolite cylinders adopt the antenna function. The light transport is made possible by specifically organized dye molecules which mimic the natural function of chlorophyll. Light shining on the cylinder is first absorbed and then transported by the dyes inside the tubes to the cylinder end. The artificial light harvesting system makes it possible to realize a device in which the dye molecules inside the tubes are arranged in such a way that the whole light spectrum can be used by conducting light from blue to green to red without significant loss. The extremely fast energy migration, the pronounced anisotropy, the geometrical constraints and the high concentration of monomers which can be realized have much potential in leading to new photo physical phenomena. We have developed two methods for preparing well defined dye-zeolite materials, one of them working at the solid/liquid and the other at the solid/gas interface.[1,2,3]



Left: Example illustrating energy migration in pyronine (donor) loaded nano crystals of about 700 nm length as observed by the oxonine (acceptor) fluorescense at different pyronine loadings p. 1, 2,..., 6 correspond to p = 0.007, 0.012, 0.03, 0.06, 0.12, and 0.23, respectively. The loading of oxonine corresponds on average to one molecule at both ends of each channel. We show the relative intensity of fluorescence spectra recordes after <u>specific excitation of only the donor</u> at 470 nm. The emission of the donor was scaled to the same hight at its maximum. The shift of the donor-emission maximum is caused by donor-donor selfabsorption and reemission.

First results will be presented to use the efficient zeolite-based light harvesting system for the developement of a new type of thin layer solar cell in which the absorption of light and the creation of an electron hole pair are spacialy separated as in the natural antenna system of green plants.

[1] N. Gfeller, S. Megelski, G. Calzaferri, *J. Phys. Chem B* **103,** 1250 (1999), ibid **102**, 2433.
[2] G. Calzaferri, D. Brühwiler, S. Megelski, M. Pfenniger, M. Pauchard, B. Hennessy, H. Maas, A. Devaux, U. Graf, *Solid State Sciences*, (2000) Volume 2, in press.
[3] M. Pauchard, A. Devaux, G. Calzaferri, manuscript in preparation.